THE BEHAVIOUR OF OIL IN FREEZING SITUATIONS

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ABSTRACT

An experimental study of the behaviour of an oil spill in a developing (grease) ice field is described. It was found that significant quantities of oil may be entrained within and beneath a grease ice field. The amount of oil entrained is increased by

i) a high oil density occurring naturally or induced by weathering.

ii) the presence of sufficient turbulence to disperse the surface oil at an appreciable rate and induce mixing within the forming ice field.

iii) a high oil viscosity occurring naturally or induced by weathering.

iv) the formation of emulsions of sea water and/or ice in the oil.

v) the formation of smaller oil droplets.

vi) the formation or coalescence of ice particles to a size of approximately 5 mm in diameter.

It is suggested that the results and observations obtained here be used as a component in an "expert system" computer model that would aid in the prediction of the fate and behaviour of an oil spill in the presence of a developing ice field and in other regimes in which oil may interact with ice. This model may then be included as part of a comprehensive model encompassing the entire spectrum of oil spill conditions which may occur in the Arctic Marine environment.

RÉSUMÉ

Dans l'étude expérimentale du comportement d'une nappe d'hydrocarbures se trouvant parmi de la glace au stade de formation du sorbet, il a été constaté que des quantités importantes d'hydrocarbures peuvent être entraînées à l'intérieur du champ de sorbet. Ces quantités sont d'autant plus grandes que:

(i) la densité des hydrocarbures est naturellement élevée ou s'est élevée du fait de leur altération.

(ii) la turbulence en surface est suffisante pour disperser les hydrocarbures à une vitesse appréciable et provoquer ainsi leur mélange avec le sorbet.

(iii) la viscosité des hydrocarbures est naturellement élevée ou s'est élevée du fait de leur altération.

(iv) il se forme des émulsions d'eau de mer, de glace ou des deux dans les hydrocarbures.

(v) il se forme des gouttelettes d'hydrocarbures plus petites.

(vi) des particules de glace d'un diamètre d'environ 5 mm se forment ou s'agglomèrent.

Il est proposé d'utiliser les résultats et les observations de l'étude pour construire un modèle informatisé de système expert qui aiderait à prédire le devenir et le comportement d'une nappe d'hydrocarbures dans un champ de glace en formation et dans d'autres situations où les hydrocarbures peuvent interagir avec la glace. Ce modèle pourrait ensuite être englobé dans un modèle plus vaste de tout le spectre des conditions auxquelles peuvent être soumises les nappes d'hydrocarbures dans le milieu marin arctique.

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1. INTRODUCTION

The exploration and development of the Arctic as an important petroleum producing region has resulted in a significant number of research programs pertaining to the presence of oil in the Arctic environment. In particular, much effort has been devoted to modeling, environmental assessment, countermeasures and recovery of oil spills in Arctic waters. However, while detailed studies have been performed and models proposed with regard to oil spills underneath ice, above ice and in open waters very little research has been performed on the topic of spills in freezing conditions, or on the interaction of oil with a developing ice field. The purpose of this study is thus to investigate and quantify the nature of the oil and developing ice field interactions. The knowledge gained with regard to this phenomena may be used to assess possible countermeasures or clean up techniques for the oil. It is also intended that the data accumulated may be used to formulate a predictive model for the behaviour and fate of oil spilled in a developing ice field.

The pertinent question in this study is that of whether, and how, oil may become incorporated within the developing or "grease" ice, hence removing it from sight and from access by most conventional recovery processes. The theory underlying the phenomenon of oil incorporation in a developing ice field is multi-faceted. An ice field's ability to retain quantities of oil within its structure below the surface of the water is presumably a function of the oil's density, viscosity and interfacial tensions as well as the thickness of the oil layer, the

porosity of the ice field and the level of turbulence present. While the subsurface behaviour of oil in water has been explored to some extent by Wilson et al. (1985) the presence of ice particles in water complicates the theory underlying this process. In the aforementioned paper it was demonstrated that significant quantities of oil may be entrained below the surface of the water if the upward buoyancy force exerted upon the oil particles is balanced by the downwards driving force of subsurface currents created by turbulence in the form of breaking waves or local downswelling regions. The upward buoyancy force may be quantified on the basis of a Stokes' Law analysis of the oil particles while the downwards force may be related to wind speeds directly above the water surface. Hence, a developing ice field or grease ice may be treated similarly with an ice/water mixture replacing water alone in the theoretical analysis. However, it is also necessary to consider the movement of the oil between the individual ice particles. This requires correlation of ice porosity and oil/ice/water interfacial tension with the wind derived turbulent behaviour of the ice/water mixture. It is also necessary to correlate this information with oil properties and the dynamic behaviour of both the oil and ice with changing environmental conditions.

It appears that the number of variables affecting the process of oil incorporation in a developing ice field is sufficiently large to render a theoretical approach to this phenomenon extremely complex and probably inaccurate and inconclusive. Thus, the initial intent of this paper is to obtain a quantity of data on the probable fate of an oil spill under freezing conditions. This empirical approach will allow the

prediction of probable oil/ice behaviour under various environmental conditions. In future, theoretical approaches may then be attempted to enhance the interpolation and correlation of experimental results.

It is intended that the results of this study may be used to aid in the development of a computer model capable of predicting the behaviour and fate of an oil spill in a developing ice field. The model would be developed empirically in a format similar to the "expert systems" now used in hospitals as diagnostic tools. Input of the quantity and physical properties of the oil as well as the existing environmental conditions into the program would yield the most probable behaviour and fate of the oil based on past observations, case studies and theory. Using the information supplied the program would then suggest further data requirements which would enable a more specific prediction of the fate of the spill. Such a program would then be capable of suggesting appropriate actions to be taken to initiate recovery or disposal of the oil.

This report thus consists of a review of the literature (Chapter 2), a description of the experimental work (Chapter 3), the results of these experiments and a field observation at Matane, Quebec (Chapter 4) a discussion (Chapter 5) and finally conclusions (Chapter 6).

2. LITERATURE REVIEW

The experimental studies and literature reviews published in the field of oil/ice interaction are focussed primarily upon oil spills under or on ice sheets. There is little work pertaining specifically to the spillage of oil on open water with subsequent freezing. However, in the course of investigating and observing oil spills in ice-infested waters several relevant observations have been reported with regard to this subject area.

The literature may be subdivided into a number of categories including

(i) the mechanism of ice formation,

(ii) oil behaviour on open water in freezing conditions,

(iii) oil behaviour in open leads between ice floes,

(iv) oil behaviour among grease ice and ice floes and pancakes,

(v) formation of oil emulsions in the presence of ice,

(vi) weathering of oil in the presence of ice

(vii) the behaviour of oil under ice.

The actual mechanism of the growth of ice in oil-free situations has been well documented. Payne et al. (1) gives a review of the initial formation of ice crystals in water, frazil ice, a slurry which increases in thickness until it attains a heavy soupy consistency referred to as grease ice. In stagnant areas the grease ice solidifies into solid "pancakes", which allows the subsequent formation of columnar ice which may reach several metres in thickness. Much work has also been performed on the mechanism of ice formation by Martin (2). However, of most

significance to this study is the observation that in its initial stages, ice forms as a slurry and is gradually compacted into thicker forms until finally a solid mass of pancake ice is produced. Also of importance is the existence of a highly porous region in the lower sections of columnar ice which has a potential for oil entrapment. In "A Field Guide For Arctic Oil Spill Behavior", Schulze (3) refers to the grease ice mixture as "spongy lumps", and emphasizes its porous nature and hence its potential to entrain oil within the body of the mixture. Martin (2) notes that the pancake ice that is eventually formed from grease ice consists of a fragile structure with many brine channels such as those found in columnar ice. This illustrates the potential of pancake ice for oil entrapment. Lewis (25) provides a review of ice formation approached from the aspect of oil movement throughout the ice structure. Thus, if the presence of oil does not significantly alter the normal ice formation process there exists the possibility that the highly porous structure of young ice may entrain significant quantities of oil.

While ice formation under Arctic conditions is well understood, the effect of an oil layer on such processes is not. The questions of whether the formation of ice proceeds through the normal frazil to grease to pancake process in the presence of oil and whether the oil becomes entrained within the ice are vital from a countermeasures point of view. Ross et al. (8) advise that while the retardation of ice growth by an oil layer will depend on the thickness of the oil layer the effect of oil on the new ice growth would be small. The insulating ability of the oil may be compensated for by the oil's ability to damp the ocean waves and thus

enhance the ice growth rate. It is then contended that the main effect of the oil layer would be to cause the formation of an oil film about the first few ice crystals which would then hamper the coalescence of the particles. After this delay period ice growth would proceed normally.

Jordan and Payne (6) note that oil on open water will alter subsequent ice formation. It is stated that a thick viscous layer of oil and grease ice will form during initial freezing stages after which normal pancake and columnar ice formation will be experienced. However, no significant effects on ice formation from the oil's presence are expected because of the positive buoyancy of almost all oils.

Walker (11) notes that while the oil would alter the albedo and emissivity of the water surface the high winds that often lead to freezing would break up a slick and thus negate the insulating effect of the oil. It is expected that the insulating effects of the oil would not be significant relative to the wind, snowfall and massive temperature drops which normally lead to quick freezing of the water. It is thus generally believed that an oil slick in open water will have little effect on subsequent ice formation.

New ice formation in open water is characterized by the slurry of ice crystals known as grease ice. Thus, understanding the behaviour of oils amongst grease ice is critical to understanding the behaviour of an oil spill on open water in freezing conditions. Payne et al. (1) cite the possibility of water and oil emulsions remaining entrained underneath grease ice and hence creating the possibility of long term entrainment with the subsequent freezing of the grease ice. In a summary of the M.V.

Cepheus spill Payne notes that much of the oil was spilled amongst a mixture of pancake and grease ice. While no actual incorporation of oil in ice was observed the apparent absence of oil slicks raised the strong possibility of oil entrainment within the grease ice.

Martin (2) performed experiments with Prudhoe Bay crude and No. 2 fuel oils combined with grease and pancake ice. It was observed that oil released beneath the ice rose up through the slurry with negligible entrainment in the ice. The grease ice was found to have a porosity of about 60% and a specific gravity of 0.99 thus making the oil's (No. 2 fuel oil) buoyancy not surprising. The oil then spread out on the surface of the grease ice and the pancake ice. The experiment also produced the observation that the surface of the grease ice was only 0.1 to 0.4 °C colder than the deep sea water temperature.

Metge (4) found that in general oil will percolate through slush ice with even the smallest agitation but in situations involving dense oils with negative spreading coefficients and high pour points, the oil may not percolate freely. More important, Metge observed that newly formed ice crystals (frazil ice) will become surrounded by an oil film which prevents adfreezing. The oil slush mixture will then slow down spreading and contain the oil.

In the C-Core report (5) on the Kurdistan incident a number of observations of the oil/ice interactions were offered. The spill of No. 6 fuel oil from the Kurdistan in Cabot Strait (March 1979) presented a situation in which the measured density of the oil was greater than that of the ice and only slightly less than that of the water. Hence it was

observed that the oil was often carried under the ice. It was also noted that the oil mixed well with brash ice. Fifty percent of the oil was believed to be entrained within the brash to a depth of 1 metre. It was estimated that the contamination level of oil in broken ice was approximately 200 ppm to an average depth of 50 cm. Of the oil blobs mixed in the brash ice drops of about 1 cm diameter composed 80% of the entrained oil. Grinding of the floes and breaking waves generated smaller and smaller drops to a diameter as small as 1 mm. These drops were uniformly distributed throughout the brash ice with smaller particles migrating to the lower part of the brash ice. It was also suggested that much of the oil may have remained underneath the brash ice. In a further summary of Kurdistan spill observations, Reimer (16) noted large quantities of oil suspended in the brash ice. He estimated that 80% of the oil present existed as blobs greater than 1 mm in diameter, distributed vertically throughout the brash ice.

Jordan and Payne (6) cited experiments with diesel oil and grease ice in which the oil was released beneath the grease ice and surfaced with no absorption in that ice. With the subsequent formation of pancake ice the oil and grease ice was forced up on to the pancakes. An experiment with Prudhoe Bay crude oil also resulted in the oil passing through the grease ice to the surface without any incorporation into the ice.

In Martin's "Anticipated Oil-Ice Interactions in the Bering Sea" (7) an in-depth description of grease ice and its formation and circulation characteristics is given. It is treated as a zone of up to

1 m depth with a region of Langmuir-like circulation and a region of no motion where the grease ice is thickening and hence in the process of forming pancake ice. In experiments performed by Martin it was found that an oil slick spilled beyond the grease ice zone and subsequently driven into the grease ice would be preferentially distributed on the surface of the grease ice and ice pancakes with only about 5-10% of the oil (Prudhoe Bay crude oil) remaining within the grease ice. This oil appeared as small, emulsified droplets derived from breaking waves breaking and circulations within the grease ice. In the same experiment it was also observed that it required on the order of several hours for the oil to surface completely through the grease ice. Hence in rapidly freezing conditions and turbulent seas a large quantity of oil could be trapped within a freezing grease ice layer. Thus the existing observations of oil in grease ice indicate minimal entrainment of oil is likely to occur unless the oil is of neutral or negative bouyancy in grease ice.

Because the formation of pancake ice is the natural progression from grease ice in the development of ice it is quite possible that an oil spill in open water in freezing conditions will encounter pancake ice, broken ice in general, as well as grease ice. A number of experiments have been performed and a number of observations have already been made of oil behaviour in broken ice. Mackay (13) reviews the expected oil/ice interactions when oil is amongst discontinuous ice. He notes that ice acts as a barrier to spreading of oil but that spreading is sensitive to oil viscosity. While viscous oils will tend to be

retained in a broken ice field light oils will spread as if the ice did not exist and will attain a normal film thickness.

Martin (7) predicts that the swell of the waves in the ocean will cause oscillation of the floes which will allow much of the spill to be pumped up onto the floe surface. However, it is predicted that a large fraction of the oil will remain trapped within the grease pancake ice system. In fact, in Martin's system only about 25% of the total oil spilled was accessible to clean up from the surface of the grease ice and ice floe. In this experiment the observation that much of the oil is trapped beneath pancakes is probably attributable to the fact that the oil was released from beneath the cakes in the experimental system. But a near-neutrally buoyant oil could easily be driven by wind, currents or waves under the floes and become trapped. In his earlier experiments Martin (2) found that the oscillating motion of the floes pumped up to half of the oil onto the ice surface. Here, the upturned rim of the ice pancakes prevented the escape of the oil. Martin (7) also notes that where floes and cakes are in close proximity to each other, in the presence of grease ice, the grease ice will inhibit oil movement between floes. Oil films were also observed on the underside of the cakes.

Deslauriers et al. (14) summarize oil movement through broken ice fields. It is surmised that low viscosity oils will penetrate ice and spread thinly over the water between floes while high viscosity oils concentrate between floes and adhere to the ice surface. It is also maintained that perhaps the largest factor in controlling oil behaviour amongst floes is ice floe concentration. In general ice floe

concentrations up to 20% act almost as an open water spill. Very little oil becomes entrained in the floes. In 20-80% ice floe concentrations low and medium viscosity oils will tend to penetrate the floes and spread thinly between them, while high viscosity oils will tend to adhere to the floes and be contained by the ice field in thick slicks. In 80-100% ice concentrations medium and high viscosity oils will be concentrated by the floes while low viscosity oils will spread thinly through the field. If there are winds and waves present the oil will be pumped along channels between the floes and up onto the floes and pancakes.

Schulze (3) concurs with the predictions of Deslauriers and also notes the ability of heavy oils to herd ice floes and increase floe concentration from as low as 20% to as high as 90% in controlled experiments.

Metge (4) notes that sudden freezes may cause the combination of many small floes into one large floe and trap quantities of oil which may not be released when the floe once again breaks apart. He also found that wind was capable of separating oil from floes for floes of sufficient size. It is also noted that turbulence driven floe motion may serve to spread heavy oils further and stretch them to a thinner film than might be expected from an open water slick. However, in general it is believed that floes will tend to restrict oil movement.

In Arctec's report on the Buzzards Bay oil spill (15) oil was observed to be transported under ice floes by the strong currents and were also incorporated into ice floes and transported significant distances by the same currents before the oil escaped. C-Core's report

on the Kurdistan oil spill noted that the pack ice contained the oil and prevented shore contamination. Oil was observed on ice floes in limited quantities as well as underneath floes. Between floes, the oil was observed to be uniformly distributed. It was estimated that 50% of the oil spilled was forced up on the surface of the floes. Schulze also noted that the oil was often carried under the ice. In agreement was evidence of oil entrapment on the underside of floes. The oil was likely dragged under the surface as a result of its near neutral buoyancycombined with strong currents. This resulted in the entrapment of the oil in the porous underside of the ice floe. Also worthy of note was the February 1970 spill of Bunker C oil from the Arrow in Chedabucto Bay, N.S. In this spill it was observed (Schulze (3)) that much of the oil was trapped between ice floes and pancakes. It was also noted that along the shoreline the ice was of a crystalline nature and that the oil grew into the crystalline structure. This consisted of small oil particles around the ice crystals and throughout the ice but usually of concentration less than 5% within the ice structure.

A spill in the Gulf of the St. Lawrence River, Canada near Matane, Quebec in December 1985 illustrated the possibility of an open water slick being driven, by winds and water currents into a field of grease and pancake ice. In this case a No. 6 fuel oil slick was driven across open water and became entrained along a shoreline field of grease and pancake ice. The grease and pancake ice were observed to contain most of the oil and subsequent ice, wind and wave forces pushed the grease ice/oil mixture up on to shore. The highly crystalline ice mixture held

large quantities of oil within its internal structure and enabled relatively simple clean up measures to be taken. Subsequent analysis of the oil by Environment Canada showed that at freezing temperatures the weathered oil was of density very close to that of the sea water in the Gulf. An oil of such density would also be negatively buoyant in a grease ice field of typical specific gravity 0.990 and therefore subject to complete and long term encapsulation in a frozen ice field. Hence, within a broken and grease ice field it may be possible for an oil slick to become entrained within or under the ice or remain on the surface of the grease ice or floes. The relative distribution of oil appears to depend on the properties of the oil as well as sea turbulence and the nature of the ice.

There is also the possibility of an open water oil spill being confined within a closing lead before frazil and grease ice formation may take place. Deslauriers et al. (14) note that closure of a lead containing oil will result in the oil being contained, forced beneath the ice, dispersed in the water or washed on top of the ice. The actual fate of the oil would of course depend upon its properties. Arctec's report on the Buzzards Bay spill (15) cites observations of opening and closing leads. Here the oil tended to flow beneath the ice as a result of wind and strong currents.

Because an oil's tendency to become entrained in frazil or grease ice is largely dependent upon its buoyancy, the possible formation of water/oil emulsions of higher net density than the oil alone is very important. Schulze (3) states that an emulsion is unlikely to occur

under Arctic conditions unless the oil has been left to weather for significant periods of time or has been exposed to a high energy environment (turbulent seas). However, tests by Science Applications Inc., (10) found emulsion formation from Prudhoe Bay crude oil after 24 hours exposure to a wave maker, although significant emulsification took longer to accomplish. Further experiments by the Coast Guard Research and Development Centre (9) produced a Prudhoe Bay crude oil emulsion of specific gravity 0.98 which would be negatively buoyant in an ice (grease, pancake) field.

Buist et al. (12) state that in rough, open seas, over a period of 24 hours, stable, viscous water and oil emulsions are formed containing 60-80% water. Payne et al. (1) and Metge (4) also noted the formation of highly stable water in oil emulsions. In particular, Payne noted that Prudhoe Bay crude oil emulsified to a water content of 50% after only 8 days in the presence of ice.

An oil spill may also increase its density through weathering. While weathering in the presence of ice has been treated in only a cursory manner a number of observations have been made on this phenomenon. In C-Core's sampling of oil in brash ice following the Kurdistan incident (5) it was found that certain light hydrocarbons were preferentially retained within the ice brash. Jordan and Payne (6), in reference to the Bouchard #65 oil spill in Buzzards Bay noted that aromatics were preferentially volatilized during weathering.

Payne et al. (1) experimented with Prudhoe Bay crude in the presence of ice and found that the specific gravity reached a steady

value of 0.98 after only two days (up from an initial value of 0.885). Furthermore, gas chromatographic analysis of the emulsified oil indicated losses of n-alkanes below n-C12. However, while completely trapped in ice the oil showed little evaporative loss. Hence it appears that the volatilization of the lighter ends of crude oil provides another route by which an oil spill may increase its density and thus increase its tendency to be entrained within newly forming ice.

While not of direct consequence to this report the behaviour of oil under sea ice is important since once an oil spill becomes entrained and trapped within an ice layer it is likely to behave as an undersea blowout would. Thorough treatments of oil behaviour under sea ice have been compiled by Dome Petroleum (17), Hoult et al. (18) ("Oil in the Arctic"), Norcor Engineering (19), ("The Interaction of Crude Oil with Arctic Sea Ice"), Martin (20) ("The Seasonal Variation of Oil Entrainment in First Year Sea Ice"), D.R. Topham (21), Wadhams (22), Keevil (23), J.F. MacLaren Ltd., (24) and Lewis (25). Also of interest is an "Oil in Ice Computer Model" developed by Wotherspoon et al. (26) for Dome Petroleum Ltd. This model predicts the distribution of an oil spill in and under sea ice.

Thus, the available literature provides an array of observations and speculations on the nature of ice growth in the midst of an open water oil slick. In general the literature indicates that a positively buoyant oil will tend to remain on the water surface and allow normal ice formation beneath it. Turbulent seas may disperse a small fraction of the oil within a growing ice field but not to any significant extent.

Less buoyant oils may be derived by weathering or emulsification or from naturally occurring dense oils and it is these oils that appear to be involved in cases of large fractions of slicks becoming trapped under ice floes or within grease ice fields. This behaviour may be compounded by turbulent seas as well as rapid temperature drops. Hence, an accurate prediction of oil/ice interaction on open water in freezing conditions will be dependent on a knowledge of the properties of the oil, the extent of weathering and emulsification of the oil, atmospheric conditions (wind velocity, temperature) as well as the possible presence of preformed ice fields.

3. EXPERIMENTAL

3.1 Apparatus

The principal experimental apparatus, illustrated in Figure 3.1 consisted of a clear lucite tank of dimensions 35 cm by 35 by 35 cm deep into which various mixtures of ice, oil and water were placed. Agitation of the mixture was obtained by use of an oscillating hoop apparatus, powered by a 12 volt battery and a D.C. motor. The hoop was constructed of a steel alloy, had a 33 cm inner diameter and could be oscillated vertically at a maximum rate of approximately 120 oscillations per minute. The vertical oscillations of the hoop, just below the surface of the water/oil interface created a low energy ripple/wave effect. The apparatus was placed within a cold room in which selected subzero temperatures could be maintained.

Photographs of the experimental runs were taken using an Olympus OM-1 35 mm camera with tungsten filament lighting.

Analysis of the various oil samples was performed using a Hewlett-Packard 5700A gas chromatograph with a Shimadzu C-R1A integrator and a 30 m x 0.75 mm I.D. glass capillary column.

3.2.1 Weathering of Oils

A mixture of 70% no.2 and 30% no.6 fuel oils was weathered over a period of several days in the presence of a grease ice field contained within a plastic tank at a cold room temperature of -5°C. Samples of the weathered oil were taken periodically and analyzed for hydrocarbon

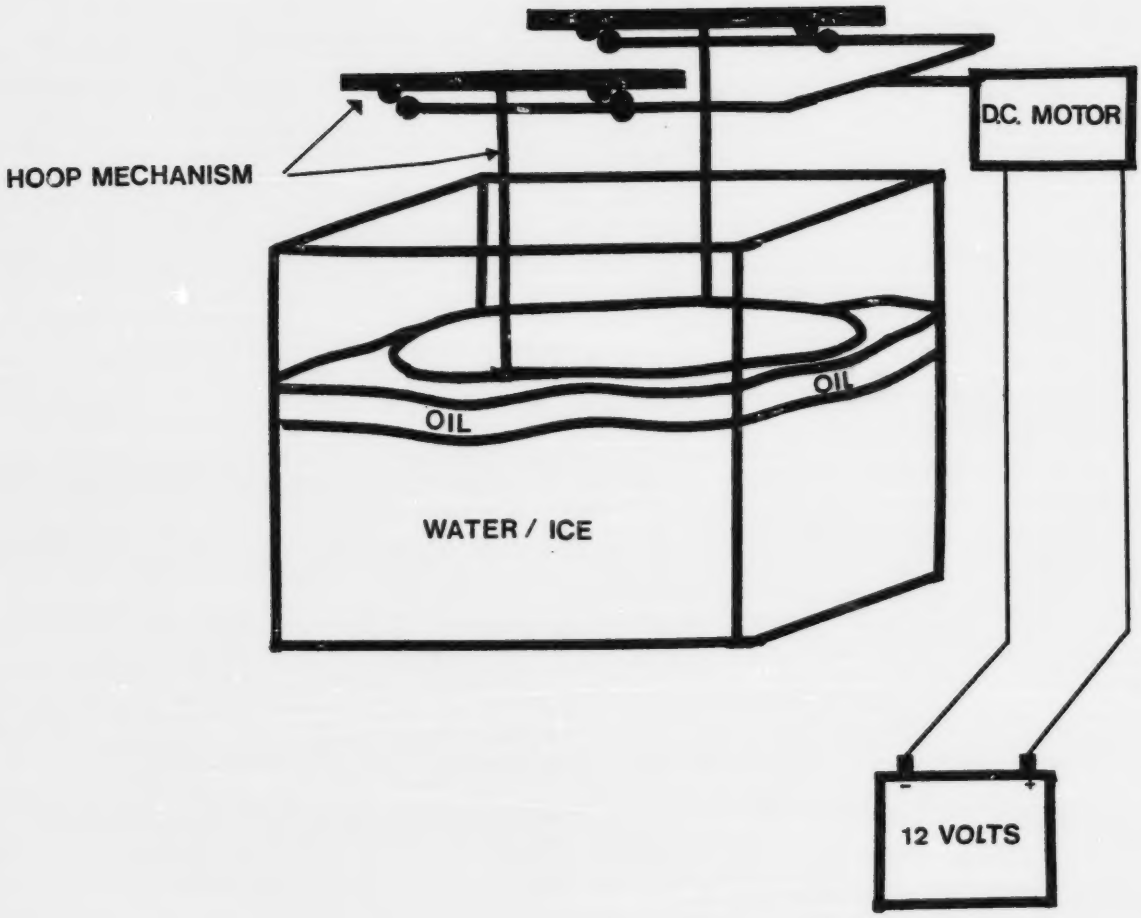

FIGURE 3.1 OSCILLATING HOOP AND TANK APPARATUS

composition and distribution by gas chromatography and also for density using a pycometer. A control sample of identical composition was weathered simultaneously in the cold room in the absence of ice and compared to the "oil in ice" sample.

3.2.2 Oil Incorporation in Grease Ice Fields

Since oil density is obviously an important parameter it was desired to test a series of oils of varying density, but of relatively constant viscosity. Unfortunately weathering a crude oil results in a marked increase in viscosity. After some investigations it was decided to use a mixutre of a light hydrocarbon oil and a dense organo-chlorine solvent. Bayol 35, a white oil, (SG of 0.790) was mixed with measured quantities of tetrachloroethylene (SG of 1.615) in order to vary the net oil density and was introduced into various grease ice fields. Oils of various densities and oil layer thicknesses were used as well as grease ice fields of varying ice particle diameter and field depths. The grease ice fields were not artificially compressed and were allowed to attain their own thickness and ice-to-water ratio. The experiments were carried out in large glass, graduated beakers of 2500 to 3500 mL volume and the oil was dyed red using Sudan Red dye in order to facilitate the observation of the oil incorporated within ice. The oil ice mixture was allowed to freeze solid after which volumes of oil incorporated within the ice could be measured. Ice-to-water volume ratios within the grease ice fields were also measured by displacement of water upon introduction of ice to the water. Fresh water was used since this greatly simplifies

the experimental procedure and some fresh over salt water stratification is quite prevalent under Arctic conditions especially in close proximity to rivers, icebergs or floes.

3.2.3 Effect of Oil on Thawing Processes

A number of experimental runs were performed in conjunction with the incorporation of oil in grease ice experiments. After oils of various densities had been incorporated into grease ice fields and allowed to freeze solid the beakers of ice and oil were placed in an ambient environment (temperature of 21° C) and allowed to thaw. Measurements of the volume of oil released as a function of time, density of oil, and extent of incorporation were obtained in order to determine the effect of the entrained oil on the thawing process. Non-oiled ice samples were also allowed to thaw in the same ambient environment in order to compare rates of thaw of oiled and non-oiled ice.

3.2.4 Effect of Emulsions

A number of emulsions were formed under freezing conditions using a rotating shaker placed in an incubator and maintained at a temperature of $-5°C$. Emulsions were created using a 70/30 combination of No. 2 and No. 6 fuel oils as well as Arabian heavy crude oil. The oils were mixed with salt water in a ratio of 90% water to 10% oil. Also, a number of samples included ice crystals of various sizes in order to investigate the possibility of emulsification of oil within a grease ice field. The rotating shaker was operated at a speed of 48 rpm over a period of 3-4

hours in order to produce the emulsions. Once formed the emulsions were introduced into grease ice fields and observed. Density and percent water content were also measured.

3.2.5 Effect of Solar Radiation

To explore the effect of solar radiation on ice formation in the presence of oil, experiments were performed in large glass tanks and at the beaker scale. Figure 3.2 illustrates the apparatus used for this set of experiments. Times were measured for initial ice formation and for the development of different thicknesses of ice in the presence and absence of light. The experiments were performed without turbulence in the water since waves tend to break up oil slicks and lessen the effect of the light radiation. Fresh water was used in the tanks and light was supplied by incandescent light bulbs of known wattage and distance from the oil. Experiments were performed in the cold room at a temperature of -5°C.

3.2.6 Effect of Oil Slick on Growth of Turbulent Ice Field

Experiments were performed in the hoop and tank apparatus using a 70%/30% mixture of No. 2 and No. 6 fuel oils with different thicknesses of oil layers in order to explore the effects of thermal insulating by the oil versus the oil's damping effect on turbulence. The hoop was operated at maximum oscillatory speed while the cold room was maintained at a temperature of -5°C. Observations were recorded and the time for

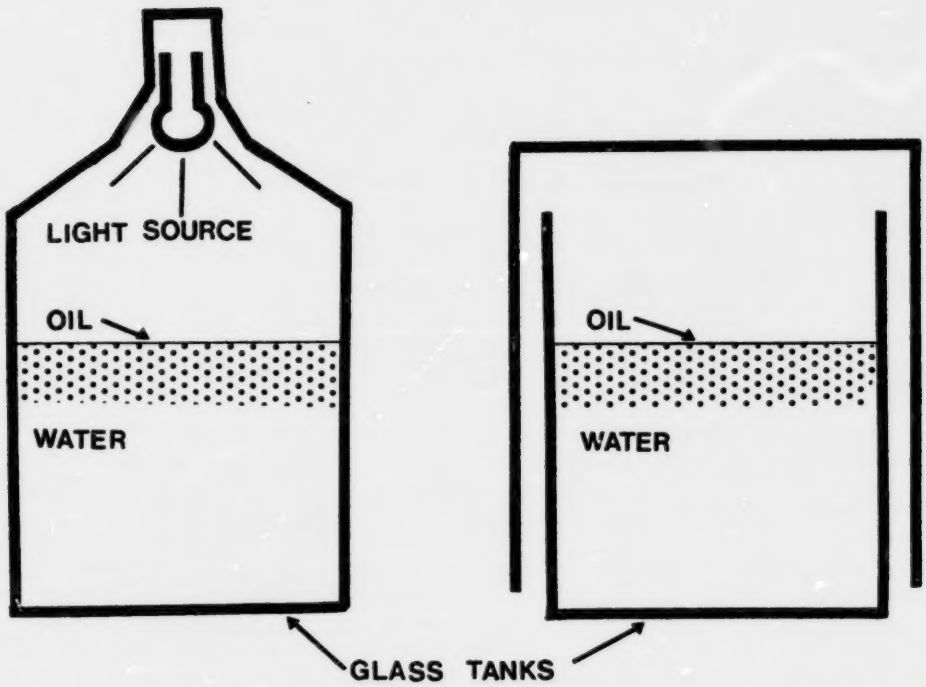

Figure 3.2 SOLAR RADIATION APPARATUS

initial ice formation was noted and compared with the time for ice formation in the absence of oil.

3.2.7 Field Study of Oil in Grease Ice

An actual spill of No. 6 fuel oil in the St. Lawrence River, Quebec, in a developing ice field, was observed in December of 1985. Oil and ice mixture samples were obtained and observed. The oil was also analyzed for density increase as a result of weathering using a densitometer at the Environment Canada River Road Laboratory in Ottawa, Ontario.

4. RESULTS

4.1.1 Weathering of Oil in the Presence of Ice

Two experiments were performed with a 70/30 mixture of No. 2 and No. 6 fuel oils. An oil layer was introduced to a grease ice field and allowed to weather over a period of 4 days in the cold room at a temperature of -5°C. At the same time a sample of the same oil was allowed to weather in the same room but in the absence of ice. Samples of the weathered oils were taken at various times and analyzed on a gas chromatograph to ascertain hydrocarbon composition. Tables 4.1.1 and 4.1.2 present the results of the analysis of the oil in ice weathering experiments as ratios of percentage composition of various n-alkanes to C_{16} alkanes. Because the oil was primarily composed of No. 2 fuel oil

Table 4.1.1 Oil in the Presence of Ice

Time (hr)	C_{12}/C_{16}	C_{14}/C_{16}	C_{18}/C_{16}	C_{20}/C_{16}	C_{24}/C_{16}
0	0.3280	1.0172	0.9593	0.6468	0.0618
10	0.3250	1.1393	0.9351	0.6320	0.0663
20	0.3357	1.1612	0.9391	0.5452	0.0641
50	0.3681	1.1198	0.9101	0.5455	0.0654
150	0.3067	0.9829	0.9212	0.5417	0.0752

Table 4.1.2. Oil in the Absence of Ice

Time (hr)	C_{12}/C_{16}	C_{14}/C_{16}	C_{18}/C_{16}	C_{20}/C_{16}	C_{24}/C_{16}
0	0.3280	1.0172	0.9593	0.5863	0.0618
10	0.3527	1.1189	0.9461	0.5983	0.0728
20	0.3462	1.0105	0.9446	0.6314	0.0781
50	0.3393	1.1369	0.8726	0.5190	0.0362
100	0.3674	1.1796	0.9279	0.7514	0.0757

and not a crude oil the oil was already weathered in the sense that it already had many of the light ends removed during refining. The results show no significant change in the C_{12}/C_{16} ratio in either test, ie. there was no significant evaporation. This was thus not a successful test of the effect of ice on oil evaporation. Another test with added lighter hydrocarbons is planned. Oil that became completely entrained within the ice was not tested but it is reasonable to assume that it would undergo even less weathering because of its lack of exposure to the atmosphere. The oil mixture had an initial specific gravity of 0.9056 and after weathering for 144 hours the specific gravity had risen only to 0.9061.

It should be noted that there was little air current or "wind" in the cold room except for occasional periods when the fan of the cooling unit became active. Thus while the actual difference in the weathering process between oil in the presence and absence of ice is minimal, barring complete encapsulation of the oil, the weathering itself appears to occur at a much slower rate than would be expected in a more temperate or outdoor environment. This result contrasts with weathering experiments performed in parallel with this study in which Alberta Sweet Blend crude oil, a very light oil, increased in specific gravity from 0.865 to 0.894 after only 50 hours in a wind tunnel at ambient temperatures. Hence, the important aspect of cold water/ice weathering is that except for very heavy crudes it would appear that weathering of any significant extent for an oil will require an amount of time that may be greater than the expected life of the spill.

4.2 Oil Incorporation in Grease Ice Fields

Figure 4.1 illustrates the results from the oil incorporation in grease ice experiment. The percent by volume of an oil layer, of known thickness, which was incorporated into the grease ice layer is plotted. Grease ice fields were obtained using ice particles of different size in order to simulate the coalescence and compaction of ice particles that naturally occur as grease ice becomes pancake ice. Hence, percent of the oil present which is incorporated into the ice is plotted against ice particle size with initial oil layer thickness and oil density as parameters.

OIL/ICE INCORPORATION

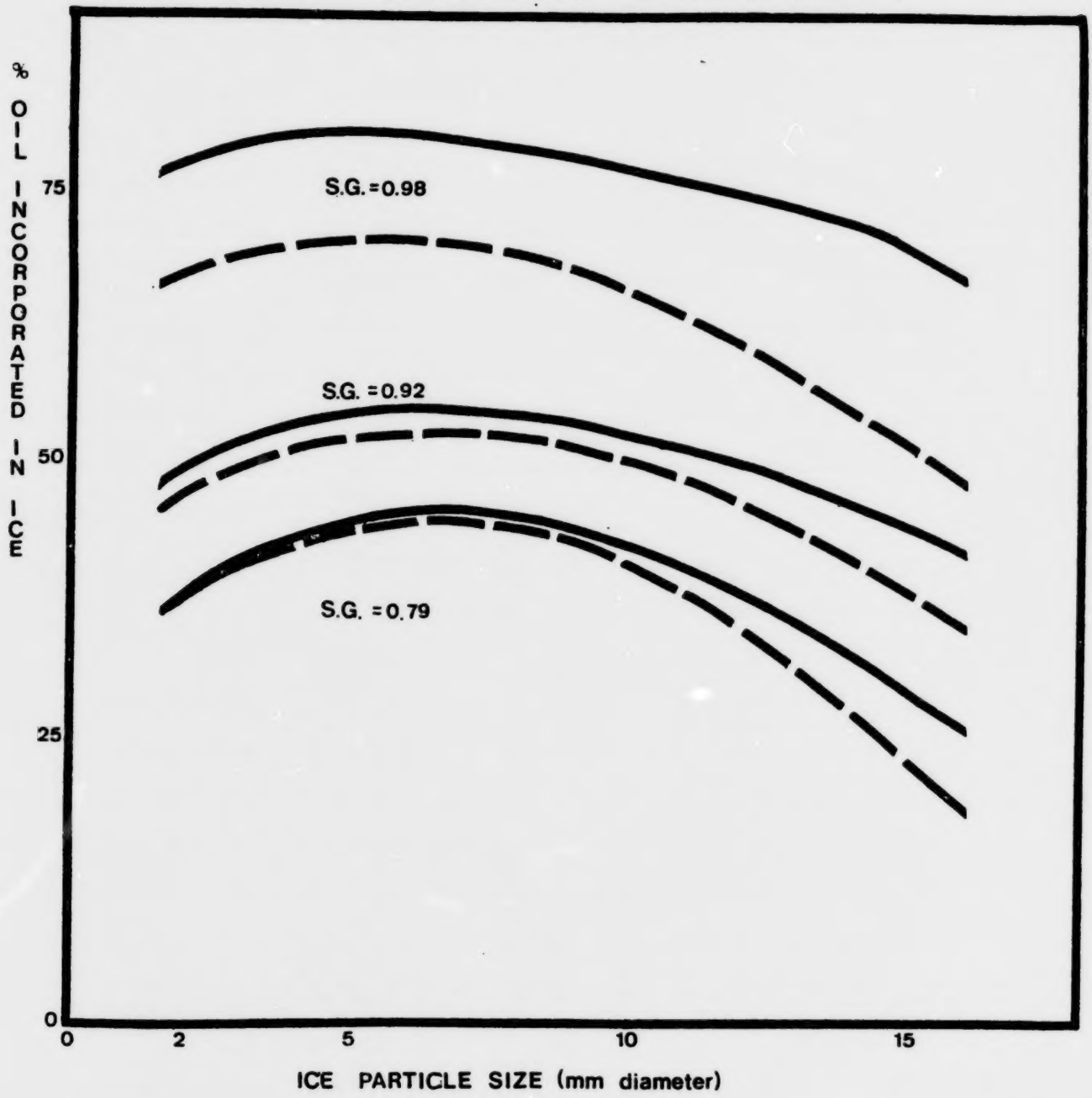

Figure 4.1 Plot of % Oil Incorporated vs. Ice Particle Size

LEGEND: OIL LAYER THICKNESS — 2 mm; - - - 5 mm

The very dense oil tested, with a specific gravity of 0.98 was incorporated into the agitated grease ice field to a maximum level of 78 percent. The oil with a specific gravity of 0.92, similar to that of ice itself, was incorporated to a maximum level of 52% while the least dense oil, with a specific gravity 0.790, was incorporated to a maximum of only 47 percent. Figure 4.2 is a set of photographs of oil of specific gravity 0.98 incorporated into grease ice while Figure 4.3 shows the incorporation for an oil of specific gravity 0.92.

The extent of incorporation appears to reach a maximum when the ice particle size is in the range of 5 mm to 8 mm. When the ice particles are very large the extent of incorporation is considerably reduced. This appears to be a result of the effect that with larger ice particles there were larger spaces between the individual particles and hence the oil was able to flow more easily to the surface of the grease field through these gaps. Less incorporation also occurred for very small ice particles (less than 3 mm diameter). This appeared to be a result of the small particles being of insufficient diameter to "trap" oil droplets below them with the result that the oil droplets pushed through and past the ice particles as they surfaced. There thus appears to be an optimum range of ice particle size where the particles are large enough to have gaps between which are sufficiently large to accomodate the oil but they are small enough to trap individual oil particles beneath them.

Intuitively, if there is a mixture of sizes of ice particles, the ice mass will offer greater resistance to oil passage because the gaps

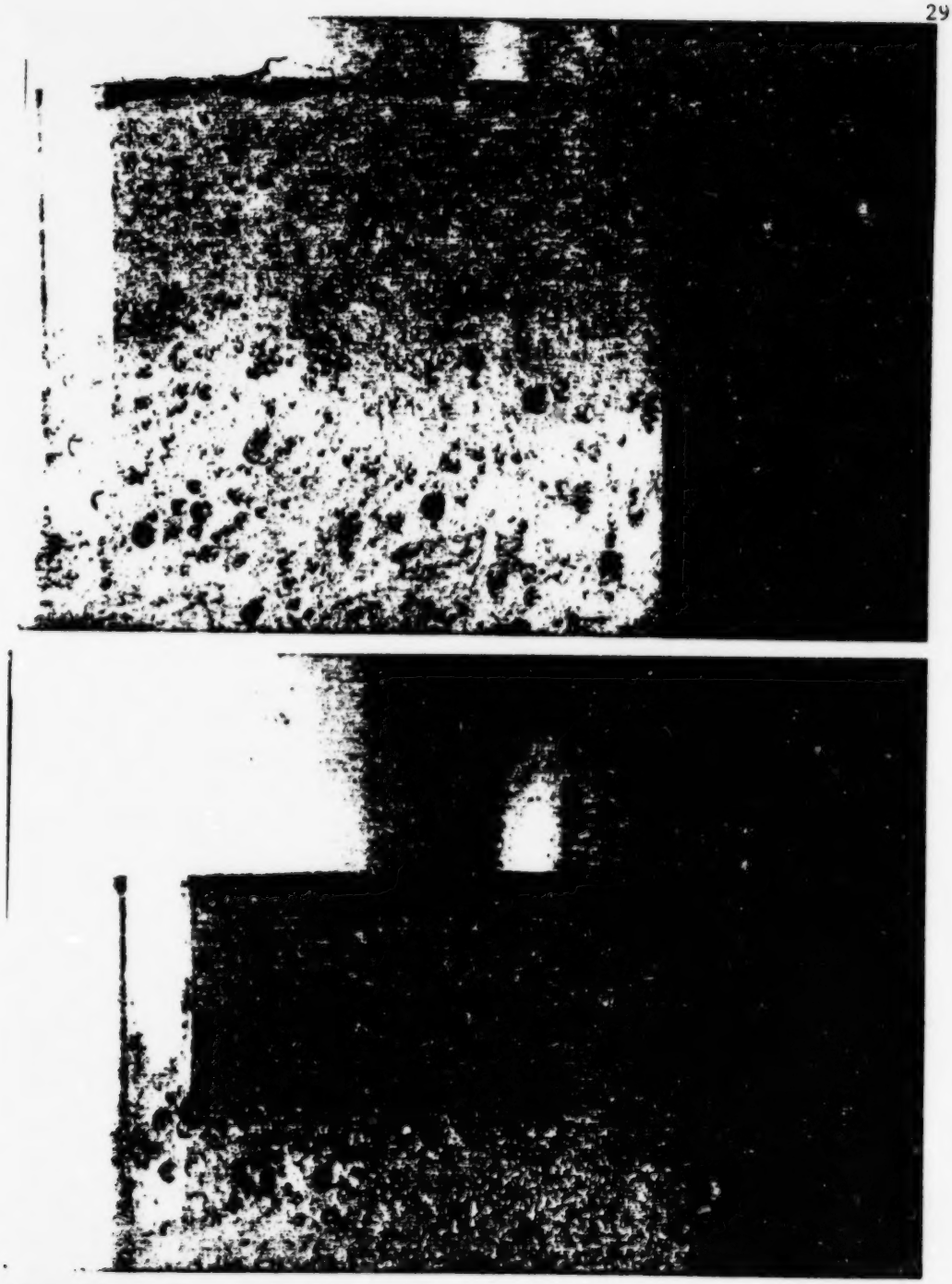

Figure 4.2 Oil (SG = 0.98) Incorporation in Grease Ice

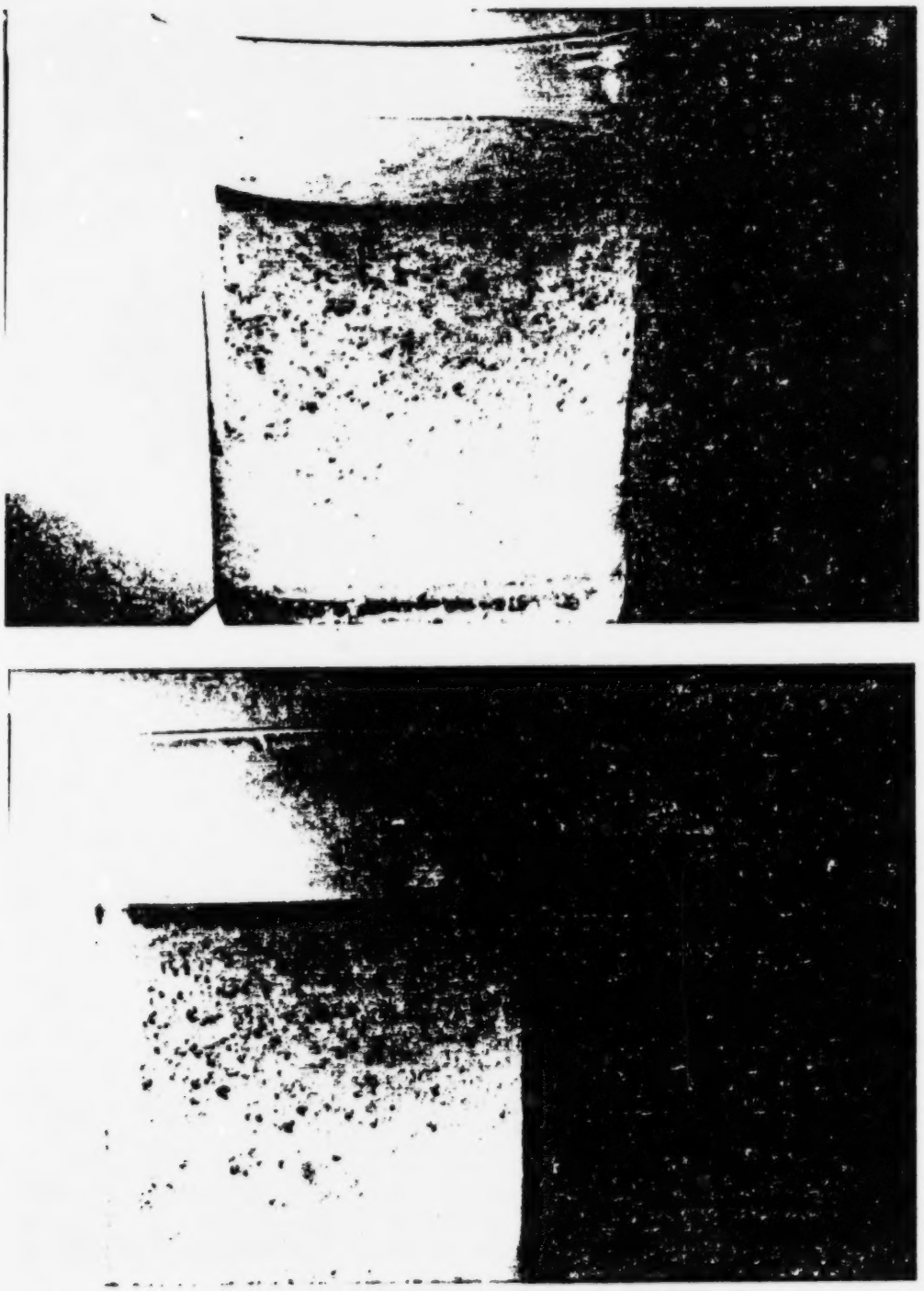

Figure 4.3 Oil (SG = 0.92) Incorporation in Grease Ice

between the larger particles may be choked with smaller particles. Unfortunately we have little information on the size distribution of ice particles which occur under actual oceanic conditions.

For the two lower density oils tested there appears to be little variation in oil incorporation as oil layer thickness increases. However for the very dense oil (specific gravity of 0.98) the amount of oil incorporated was reduced significantly with increasing oil layer thickness. This result appears to be related to the effect that as thicker layers of oil were introduced, the oil droplets (which dispersed throughout the grease ice as a result of agitation) tended to be much larger than those created with a thin oil layer. The thick layer drops tended to be on the order of 4 mm to 6 mm diameter while the thin layer drops were on the order of 1 mm to 3 mm diameter. Because the thick layer oil droplets were much larger their positive buoyancy driving force was greater than that for small droplets.

It appears that a simple"rule of thumb" is that the oil droplet size will be similar to the thickness of the oil slick from which they were derived.

4.3 Effect of Oil on Thawing Processes

The results from the thawing experiments are illustrated in Figure 4.4 as a plot of percent oil remaining incorporated within the ice as a function of the time that the oil-ice mixture has been exposed to an ambient environment. Oil density is the parameter.

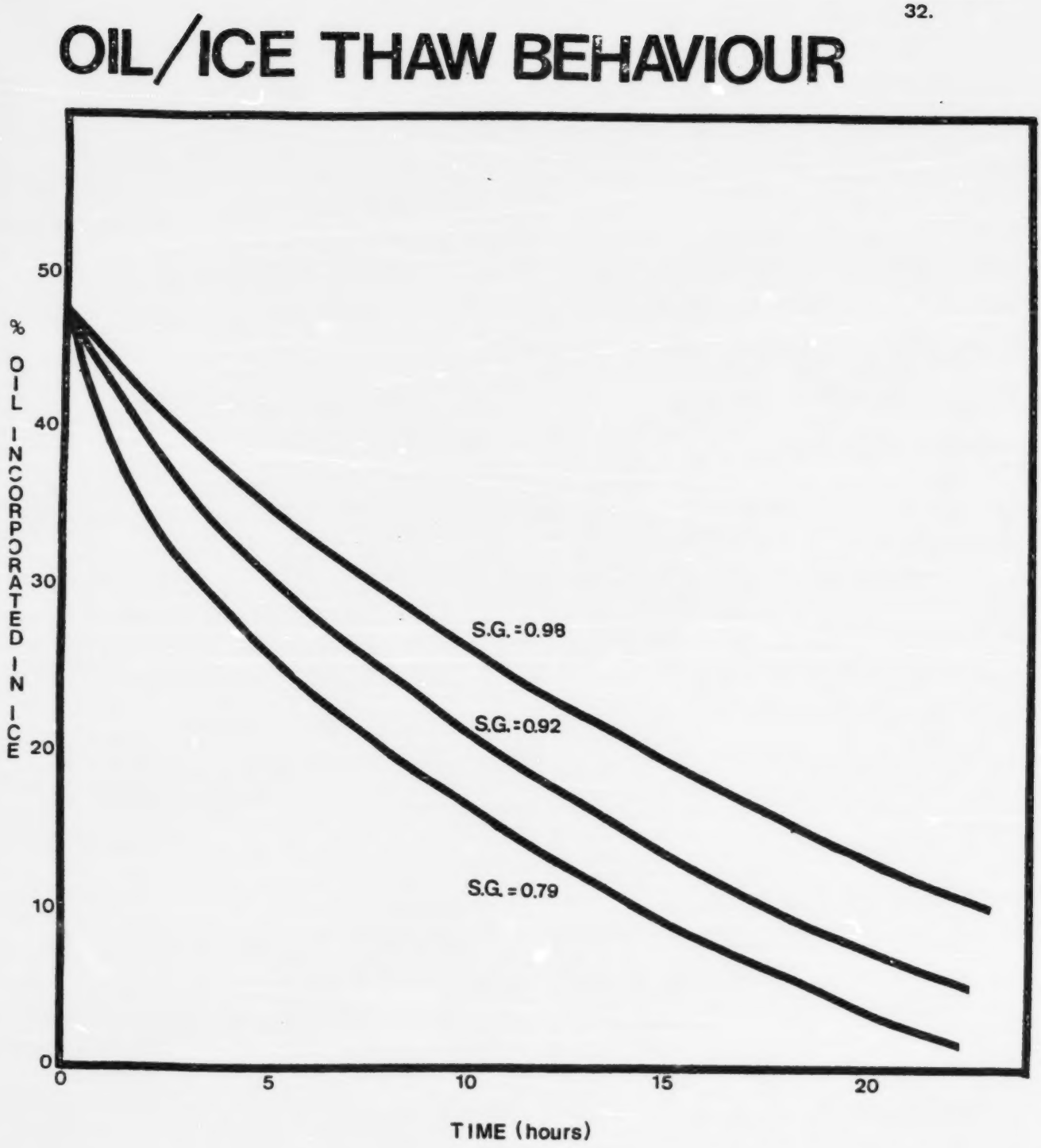

Figure 4.4 Plot of % Oil Incorporated in Ice vs. Time During Thawing of Oil/Ice Mixture

When ice forms the thickness of the ice increases proportionally to the square root of time. This is a result of the growing ice insulating the water beneath it from the cold environment above it. Hence, as the ice gets thicker more time is required for further ice formation. However when ice melts it does so primarily from the top down. The resulting water layer is not able to insulate the ice from the warm environment in a manner analogous to the freezing mechanism since the ice is less dense than water causing the water layer to drain from the ice surface. This results in a decrease in ice thickness proportional to time. Hence the near linear decrease of the amount of oil incorporated with time is not unexpected providing the oil is dispersed fairly evenly within the ice layer. It was observed that the oil was quite evenly dispersed throughout the first 9 cm of ice and since the ice melts from the surface downwards the oil was released proportionally to decreasing ice thickness.

The deviation from linearity of the plots after as short a time as 5 hours is likely a result of the growing oil layer on top of the ice. Because the oil was less dense than the ice it remained on top of the ice once released from within the ice. The oil then insulated the ice from the warm environment and retarded the rate at which the ice thaws and hence slows down the rate at which oil is released from the ice.

The curves plotted show that the denser oils required significantly larger amounts of time to be released from the ice. There are several possible reasons for this. Because the denser oils were less buoyant in the grease ice field it was possible for the downward driving force exerted by the agitation of the ice to force the oil

droplets down to the greater depth within the grease ice field. Consequently it required more time for the ice to melt sufficiently to allow the most deeply entrained oil to be released. In a naturally occurring sea ice field the freezing process causes the expulsion of salt from the ice. This process results in the formation of brine (salt water) pockets and channels within the ice. During the thawing process these pockets and channels often become joined together to create continuous pathways through the ice. Hence, for oil trapped in sea ice these brine channels become an important pathway by which a positively buoyant oil may reach the surface of the ice. However, because of a denser oil's near neutral density its upward migration through the channels is slowed down. Furthermore, because the oil is entrained to a deeper depth it has farther to travel to the surface and more time is required to form drainage channels from such a depth to the surface. The denser oils also have a slower Stokes' Law rising velocity.

Exploratory experiments were performed to observe the effects of oil incorporation on the actual rate that the ice thaws. However, in no case was the oil layer completely incorporated within the ice and hence the situation reverted to the case of ice with an oil film above it which has previously been studied by other authors.

4.4 Cold Emulsions

An emulsion of Arabian heavy crude and salt water was formed which had a net specific gravity of 0.946 and was composed of approximately 40% salt water and 60% oil. The emulsion was obtained after three hours of

shaking at 48 rpm. It is possible that more vigourous or longer shaking would have produced a higher water content and hence higher specific gravity emulsion. The emulsion was not highly stable and remained in emulsified form, in the absence of ice, for only about 50 hours.

The emulsion was poured into a grease ice field within a 3500 mL beaker and stirred. Figure 4.5 is a series of photographs of the resulting emulsion in ice incorporation. While the exact extent of incorporation was not measured the lack of oil on the surface indicates incorporation far greater than that exhibited by oils of the same specific gravity in previous experiments. Hence, a significant factor in oil incorporation within ice appears to be the viscosity of the oil. While the oils used in previous experiments were quite dense they had low viscosities since they were composed of a mixture of a low viscosity white oil mixed with low viscosity tetrachlorethylene. Such a mixture retains its low viscosity at low temperatures. Conversely, crude oils and their emulsions tend to increase greatly in viscosity with decreasing temperature. It was observed that the oil bubbles incorporated within the ice field were much larger than those formed using low viscosity oils. The high viscosity oil droplets were as large as 10-20 mm in diameter. Continuous agitation reduced many of the oil droplets to a size as small as 5 mm in diameter. However, the relatively large size of the emulsified oil droplets prevented their movement upwards through the ice field. An estimate of the amount of oil incorporated was obtained by pouring the remaining surface layer of oil into another beaker. The

Figure 4.5a Water-in-oil Emulsion Incorporated in Dense Grease Ice.

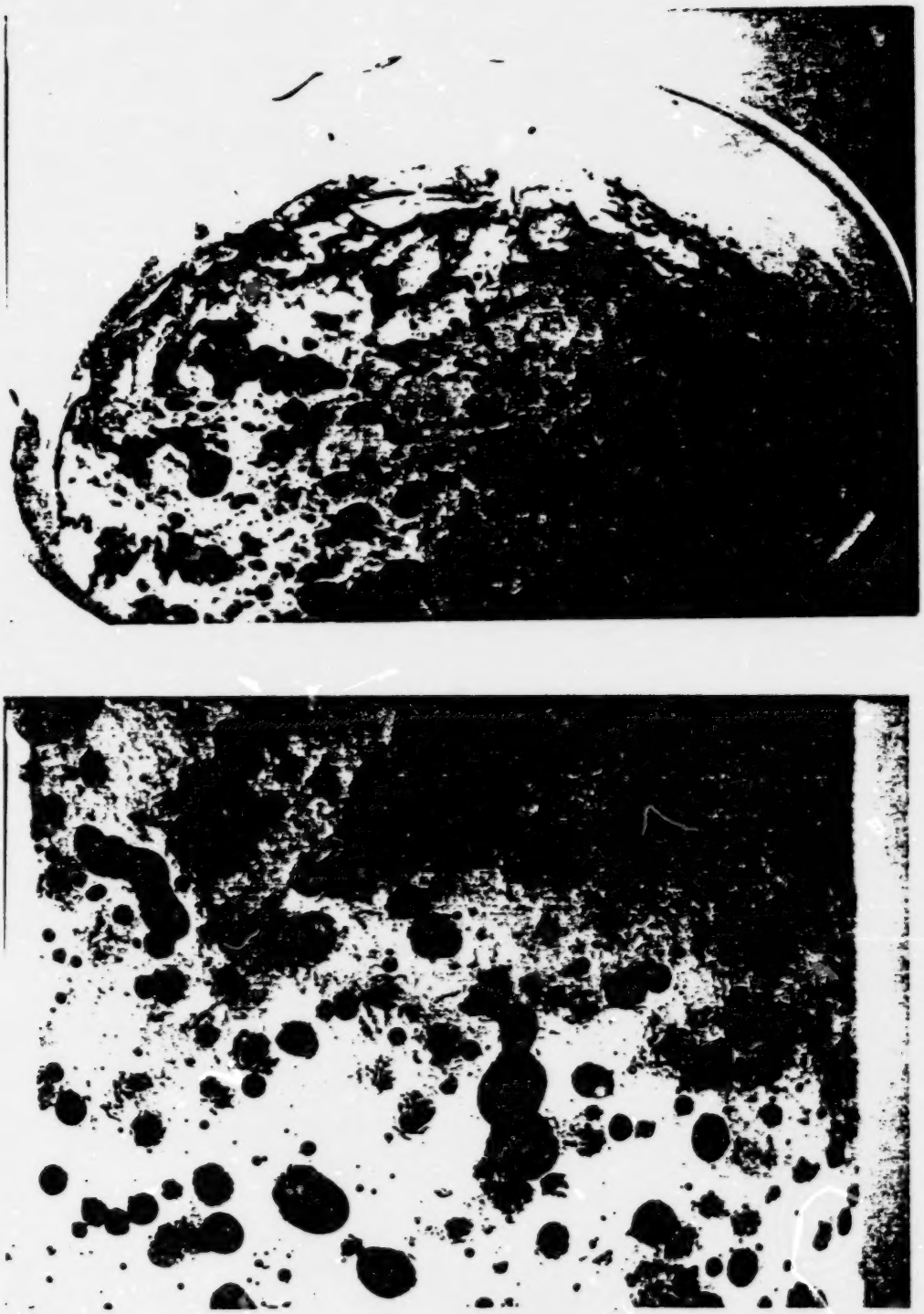

Figure 4.5b Water-in-oil Emulsion Incorporated in Dense Grease Ice.

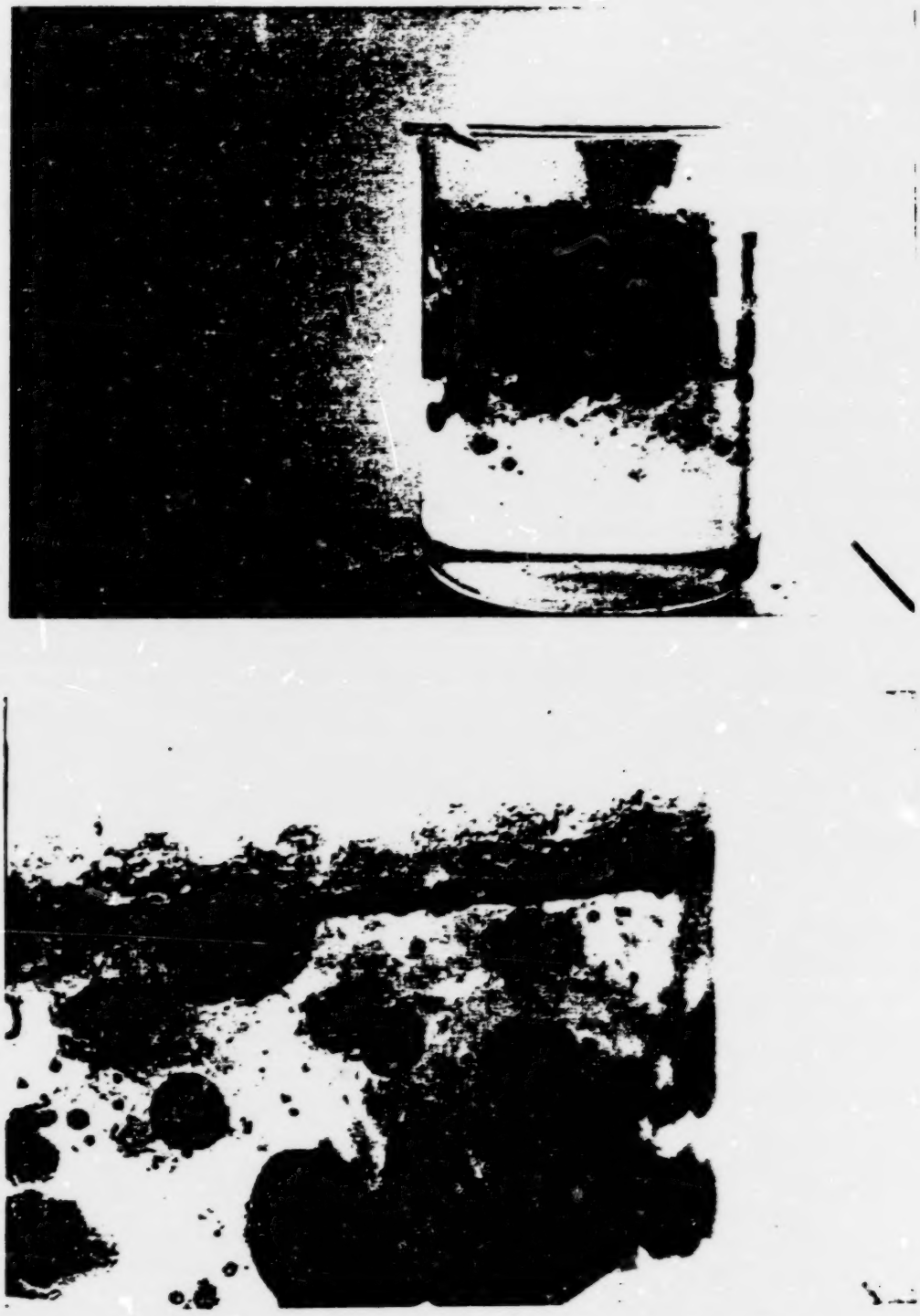

Figure 4.5c Water-in-oil Emulsion Incorporated in Porous Grease Ice.

Figure 4.5d Water-in-oil Emulsion Incorporated in Porous Grease Ice.

amount of oil incorporated was measured as 80% to 90% of the initial quantity.

The photographs given in Figure 4.5 also illustrate the emulsion/ice mixture in both densely and thinly packed grease ice fields. The oil droplets in the ice field of greater porosity were significantly larger than those occurring in the more densely packed ice field. While the oil droplets in the thinly packed ice were almost exclusively in the 10-20 mm size range the oil droplets in the more densely packed ice field were in the 5-10 mm size range. It appeared that the stirring of the oil ice mixture within the beaker caused greater grinding motion between ice particles in the denser ice field than in the less porous ice field. This resulted in increased splitting of oil particles and hence the smaller oil droplets.

An emulsion was also created using a 70/30 mixture of No. 2 and No. 6 fuel oils, salt water and ice particles of approximately 2 mm diameter. The oil/water/ice volume ratio before emulsification was 1:9:1. However, it was not possible to obtain an oil/water ratio after emulsification or a net density of the mixture. The emulsion required 8 hours of shaking at 48 rpm to achieve even a very unstable emulsion. Observation of the shaking apparatus revealed that the presence of the ice particles appeared to dampen the shaking motion and hence retard the emulsification process.

Once incorporated into the grease ice field, both the Arabian Crude oil and No. 2/No. 6 fuel oil emulsions were observed over a period of 48 hours in order to detect any deterioration of the emulson. Over

this time period no separation of oil from water was observed with the ice incorporated emulsions.

4.5 Effect of Solar Radiation on Ice Formation

The experiments performed on the effect of solar radiation on ice formation, as described in the experimental section, yielded few useful results as a result of variable temperatures within the cold room. The oil used was a 70/30 mixture of No. 2 and No. 6 fuel oils. Circumstances dictated that the cold room be maintained at a temperatuare of -5°C. At this temperature, a 60 watt light bulb, positioned 1 m above the oil layer of 2 mm thickness, provided sufficient radiation to prevent the formation of ice beneath the oil over the 24 hour observation period. The insulated tank, also with a 2 mm layer of oil over water, but kept in the absence of light showed individual ice crystals being formed within an hour. A complete ice layer underneath the oil was formed after 4 hours and the ice layer was a full 10 mm thick after 12 hours. The results obtained are also somewhat in question because of the frequent thaw cycles that the cold room requires during which the cold room temperature rises to just below 0°C.

4.6 Effect of Oil on Growth of Turbulent Ice Field

Tests were performed using the principal experimental apparatus and a 2 mm layer of the 70/30 No. 2 and No. 6 fuel oils mixture. Turbulence was provided by the oscillating hoop mechanism. While the expected frazil/grease/pancake ice formation was not noted a slushy,

crystal-like porous frozen mixture initially formed which trapped significant quantities of oil within its internal structure. Below this layer columnar ice formation was observed and in the first few cm of columnar ice round oil droplets of varying diameter became trapped within the growing ice. The growing crystals of columnar ice are illustrated in Figure 4.6. The droplets of oil ranged in diameter from as small as 0.5 mm to as large as 10 mm. The upper layer of the ice/oil mixture was solid but porous in nature as may be seen in Figure 4.7 with the pores in the ice containing significant quantities of oil. During the early period of the freezing process the oil was wave driven downwards by the hoop and would then resurface due to its positive buoyancy in the water. However, as freezing progressed the ice chunks formed and then broken by the hoop became more numerous and hence formed a thicker mixture in the oil and water. This broken ice increasingly inhibited the ascent of the oil to the surface. However the oil of initial specific gravity 0.919 was sufficiently close to neutral buoyancy to allow the entrainment of large quantities of oil within the first 10 cm layer of water and ice by the downward motion of the hoop. Shortly thereafter the ice and water mixture was of sufficient consistency to trap even large droplets of oil and also allow the formation of columnar ice around and beneath the oil. The resulting oil-ice mixture was of porosity such that when pressure was exerted downwards upon it oil would flow upwards through pores and channels within the ice.

As described in the literature review the bottom edge of columnar ice formation is very porous and fragile and consists of vertical fingers

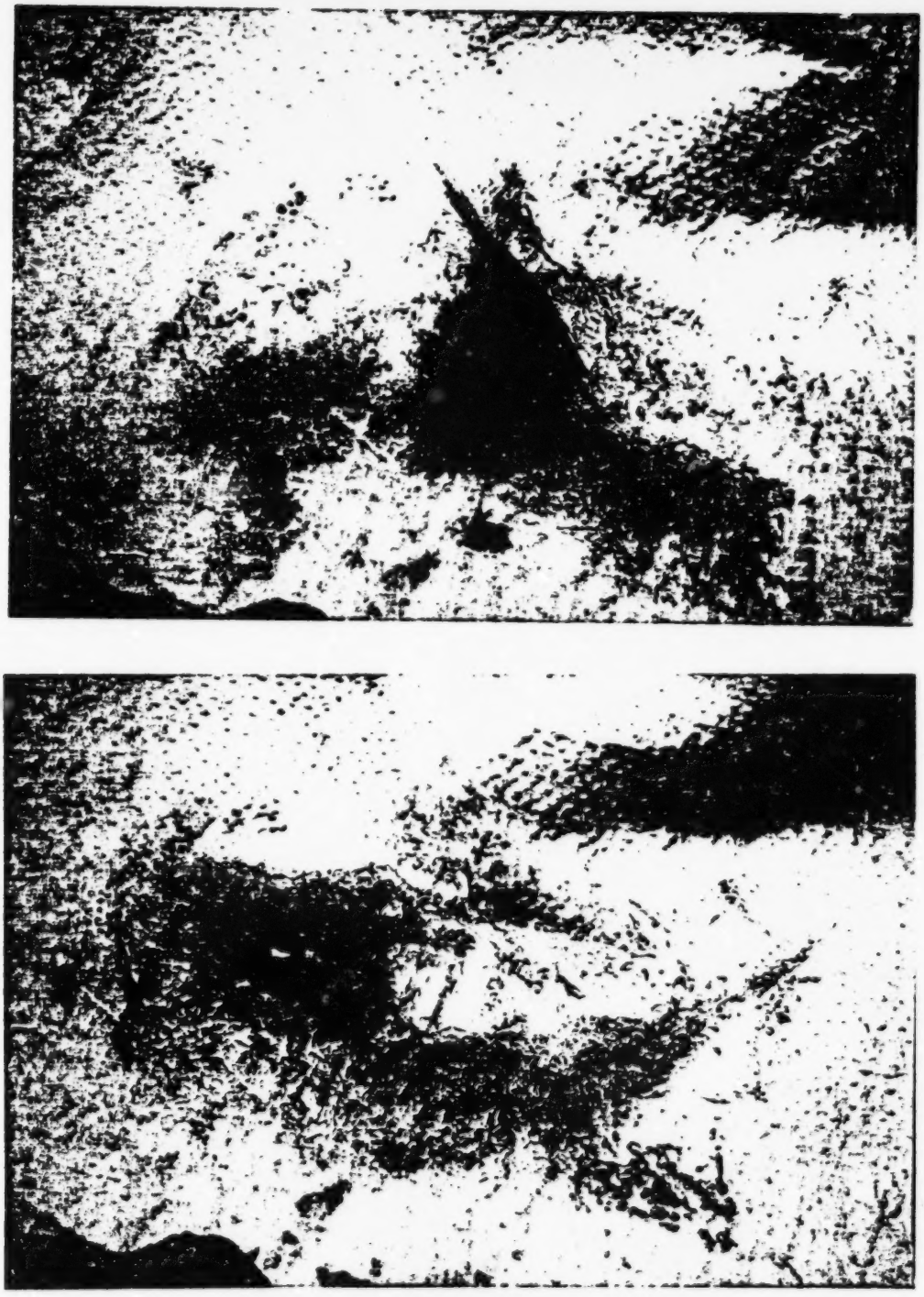

Figure 4.6 Crystals of Young Columnar Ice

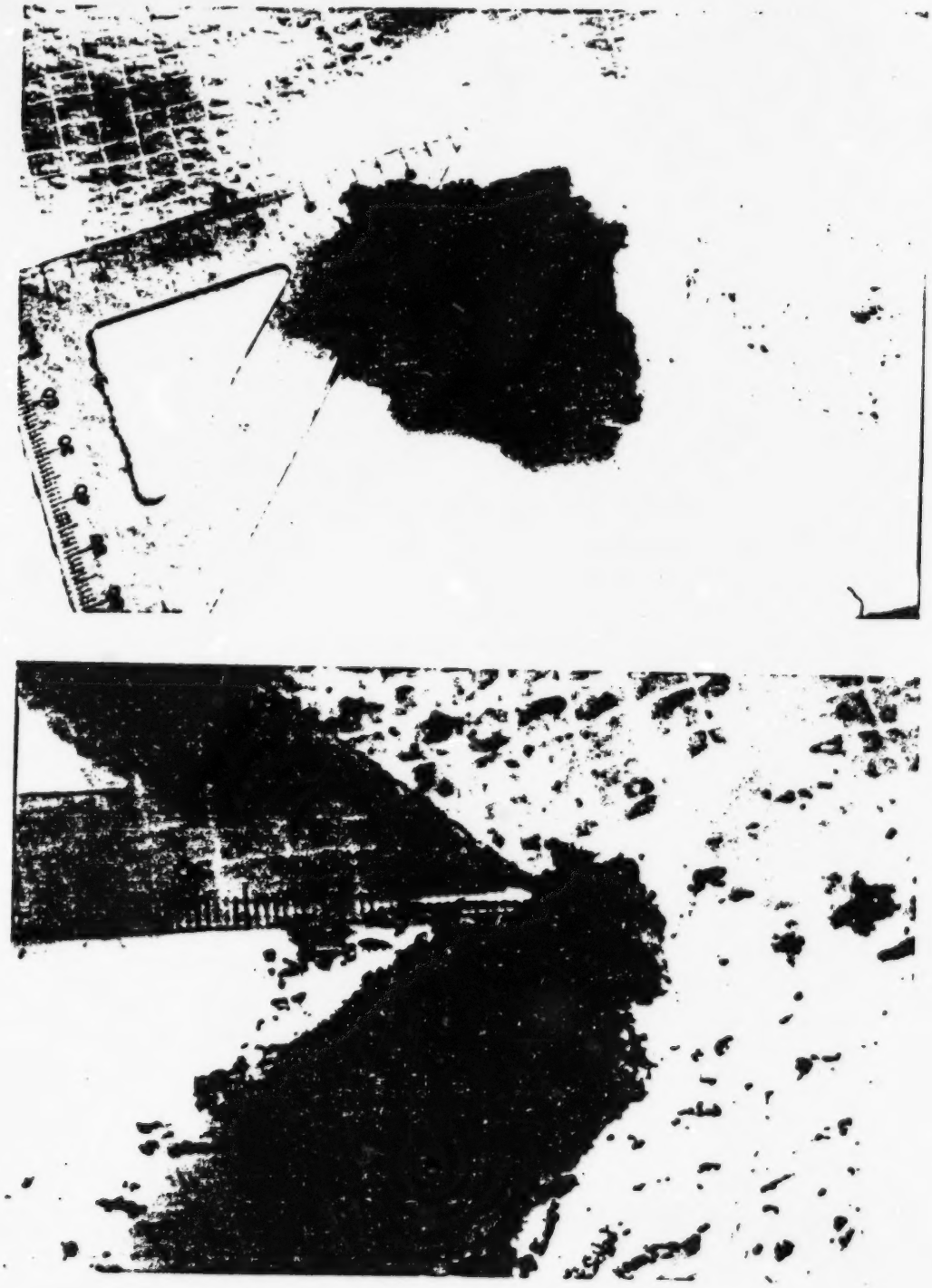

Figure 4.7a Porous Oil/Ice Mixture

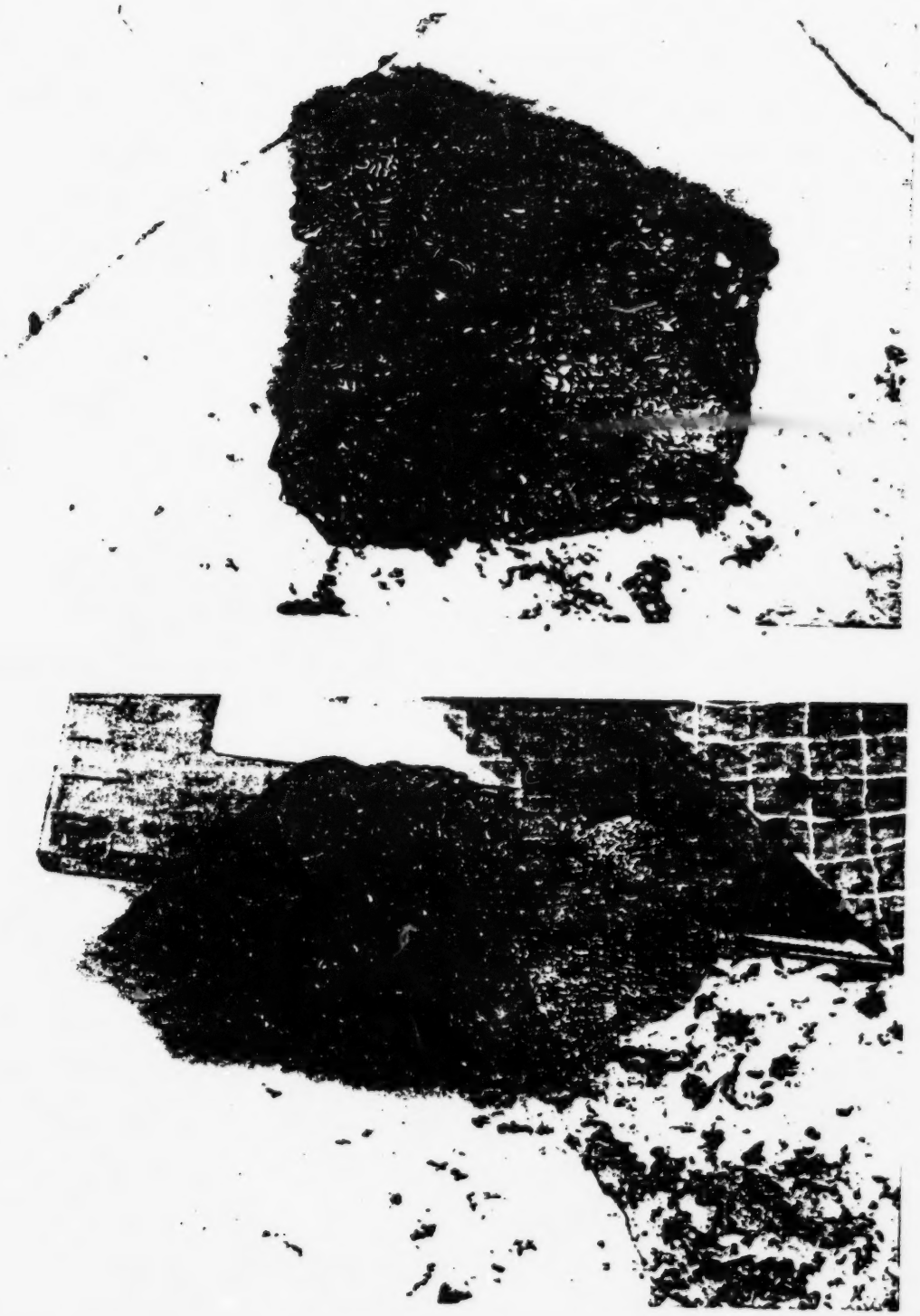

Figure 4.7b Porous Oil/Ice Mixture

of ice crystals which collapse upwards onto a horizontal plane and form plates of ice. During the process of initial columnar ice formation, oil driven downwards by the hoop became entrained between the collapsing ice fingers to create the aforementioned porous oil/ice mixture. Once columnar ice formation had begun oil droplets were driven below the ice through areas where columnar ice formation had not begun. Such oil droplets appeared as isolated drops within the columnar ice. This is illustrated in Figure 4.8.

The same experiment was performed using Bayol 35 oil which is a white oil of low viscosity and a specific gravity of 0.790. The oil was dyed red to facilitate observation of oil entrainment in the ice. As with the denser oil the oil was driven downwards by the wave motion of the hoop but because of the oils greater buoyancy it rose much more quickly than the fuel oils and tended to surface even when ice formed and became a very thick broken ice mixture. As a result only a very small amount of oil actually became entrained within the ice and almost no oil was entrained within the columnar ice below the broken ice. No porous crystal ice as in the previous experiment was observed. Some small droplets of oil became entrained within the first few centimetres of the broken ice and at the broken/columnar ice interface. However these drops were neither of the same size nor quantity as the fuel oil droplets. The droplets were entrained to a much shallower depth than the fuel oil droplets as well. This behaviour is illustrated in the set of photographs in Figure 4.9.

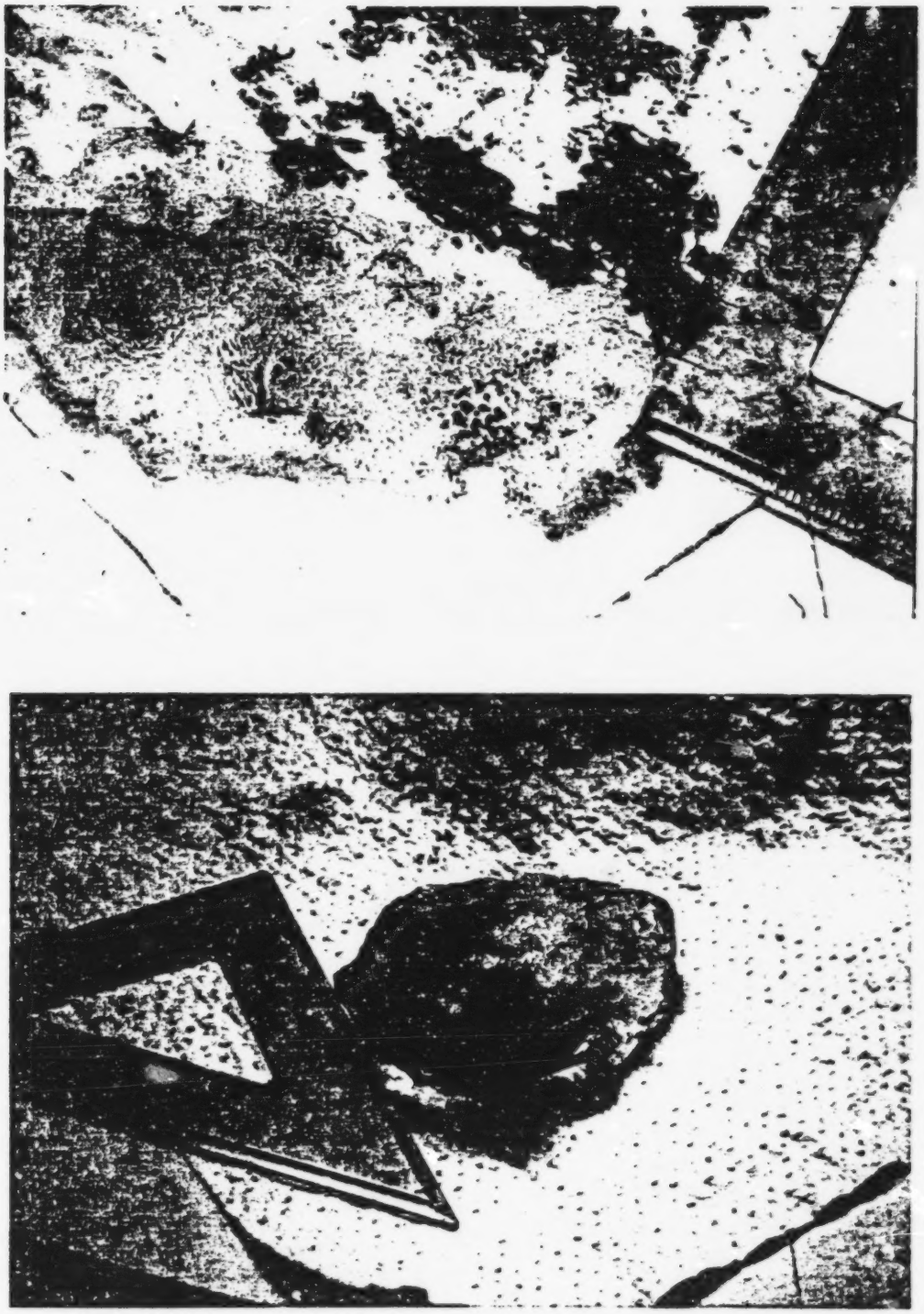

Figure 4.8a Isolated Oil Drops Within Columnar Ice

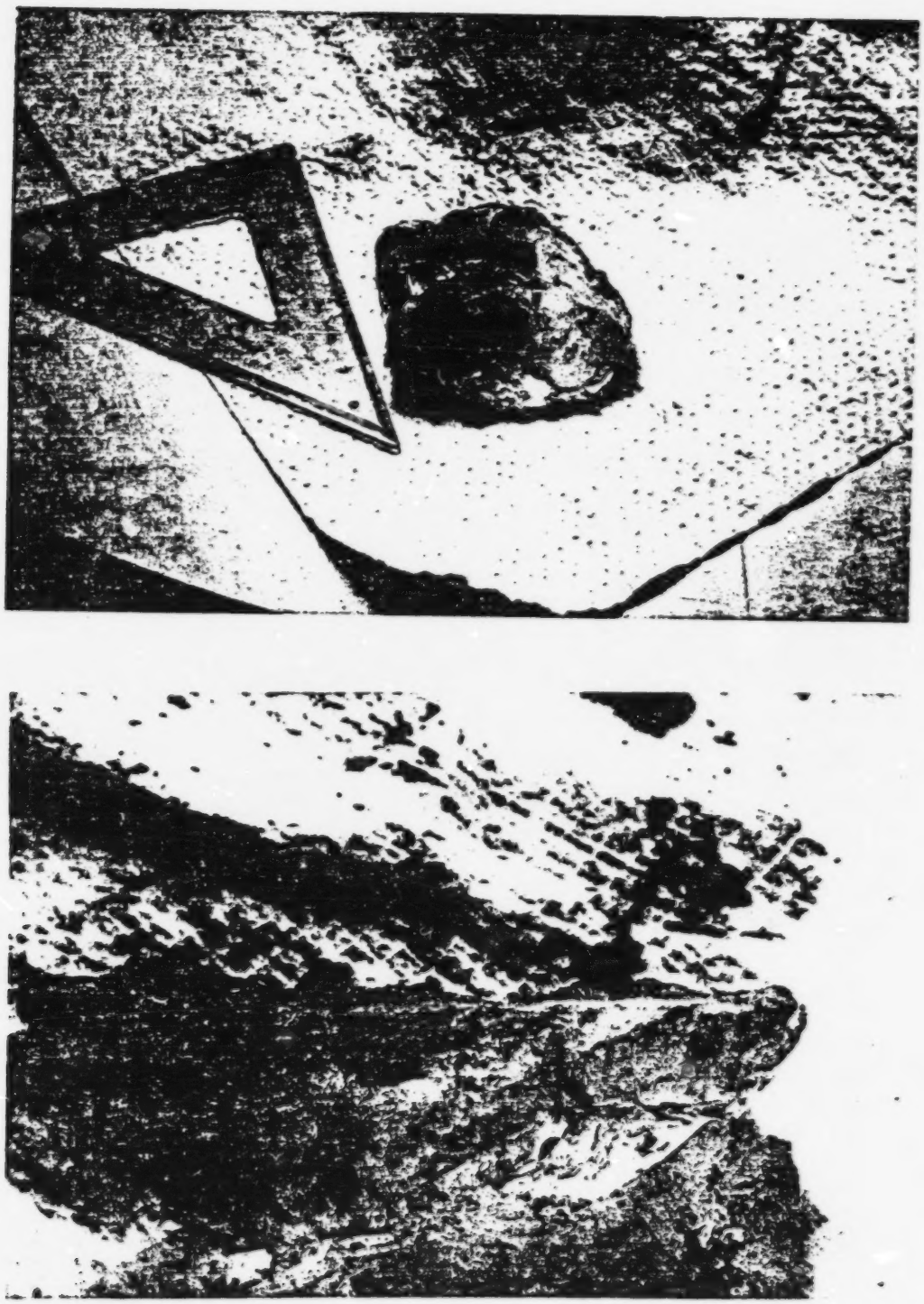

Figure 4.8b Isolated Oil Drops Within Columnar Ice

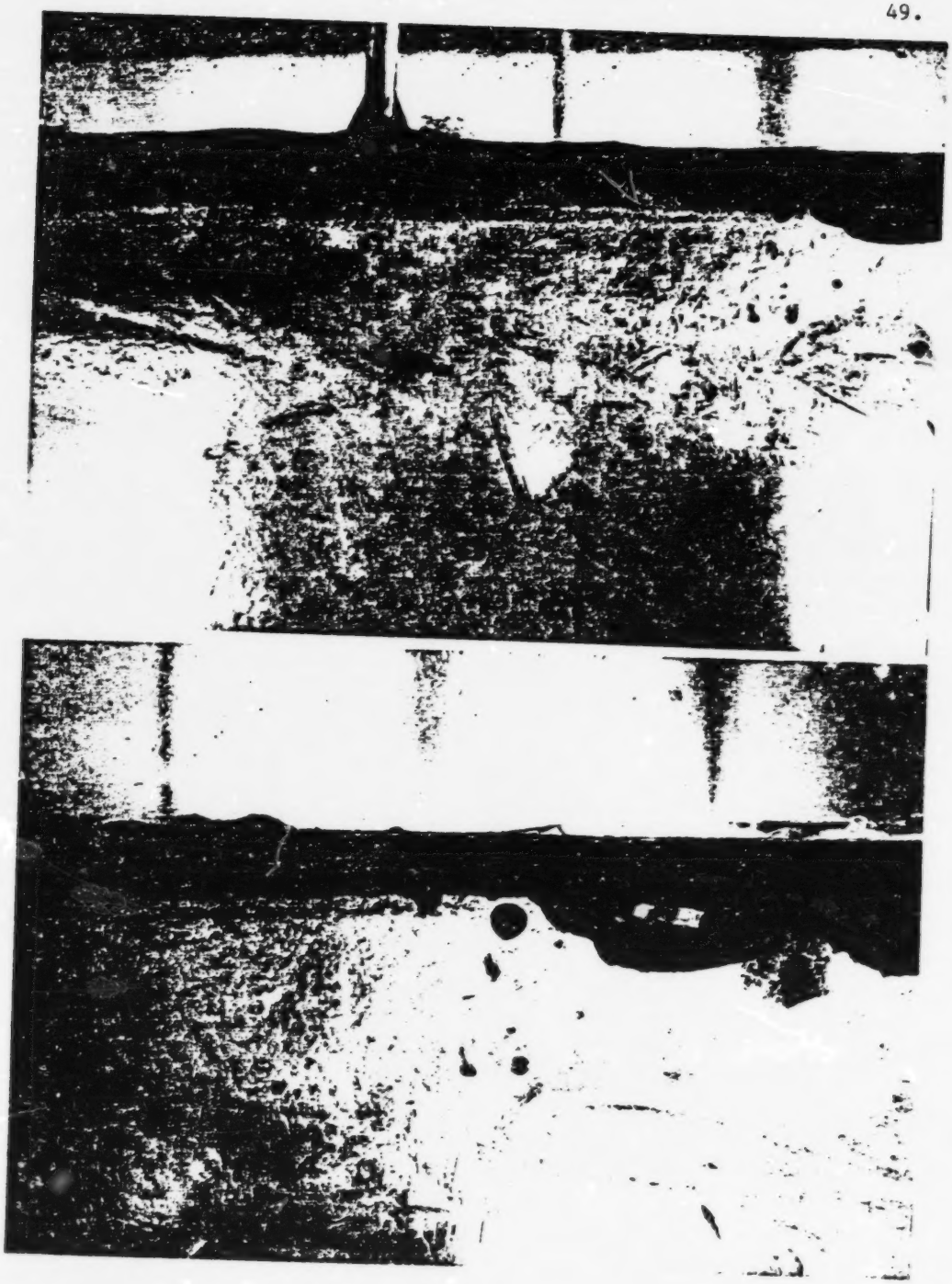

Figure 4.9a Oil (SG = 0.79) Incorporation in Turbulent Developing Ice Field

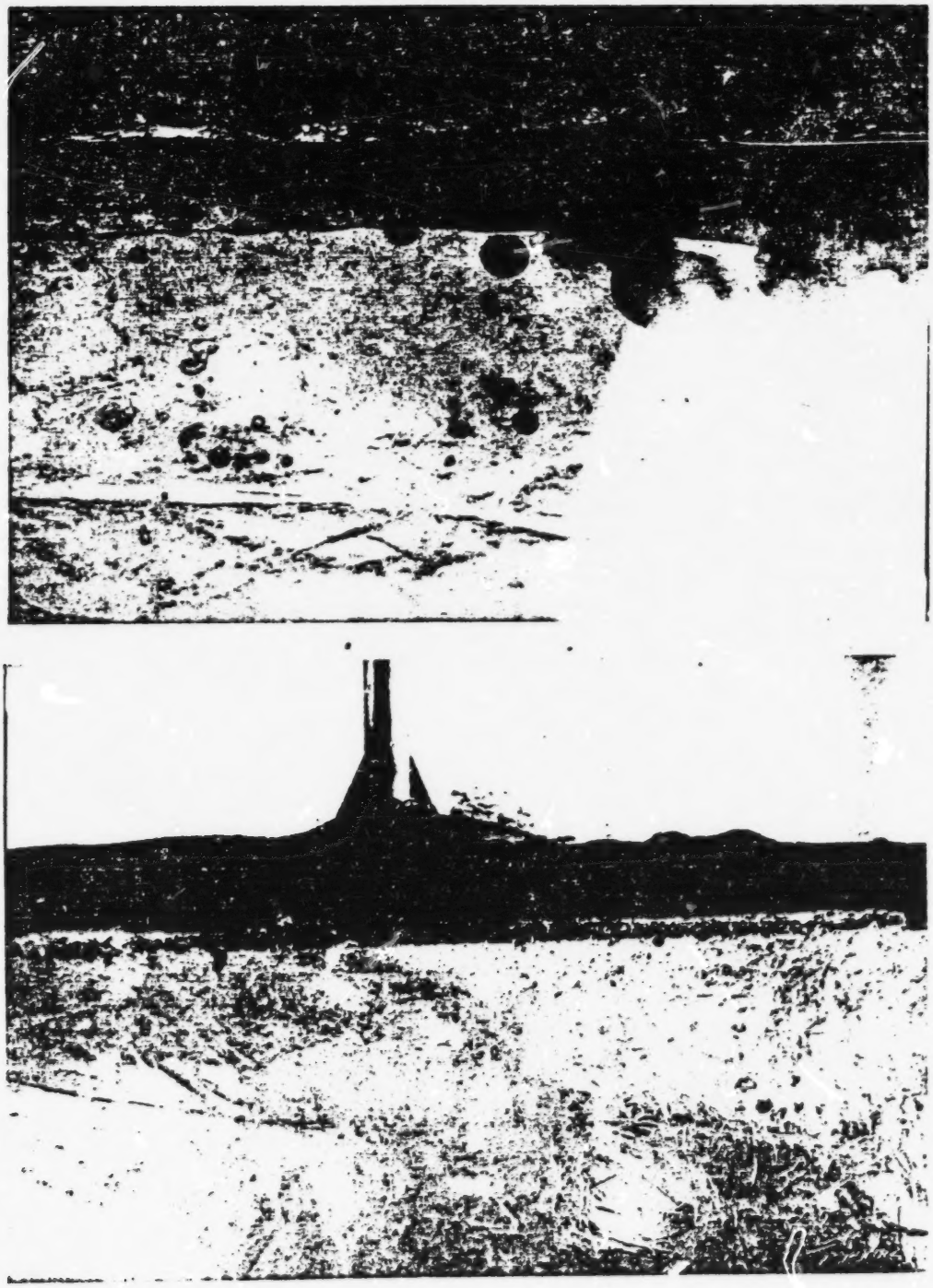

Figure 4.9b Oil (SG = 0.79) Incorporation in Turbulent Developing Ice Field

The wave or ripple effect produced by the hoop was not of sufficient energy to break up the oil layer except about the actual perimeter of the hoop. Because of this it was not possible to quantify the balance between the oil's insulating, ice growth retarding behaviour and its wave dampening, ice promoting behaviour. Also, solar radiation was not introduced to the experiment. It is probable that solar radiation would add to the insulating effect of the oil and further retard ice development. However, the experiments performed support the suggestion that the oil layers of thickness that would be expected in an actual spill would not be of sufficient depth to dampen swells of the magnitude expected in an ocean. Oceanic wave action is expected to break up the oil slick and hence severely retard its ability to dampen waves and insulate the water below from the subzero atmosphere. While the times recorded for wave formation are not believed to have a high degree of accuracy there was no significant difference between time for ice formation in the presence or absence of a thin oil layer under turbulent water conditions.

It would be interesting to conduct a heat transfer rate analysis to elucidate the nature and extent of the effect of oil on freezing and thawing rates with and without radiation.

4.7 Field Study of Oil in Ice

As noted in the literature review a spill of No. 6 fuel oil occurred in the Gulf of St. Lawrence River in December of 1985. The author was able to travel to the site of the spill and arrived three days

after the spill had occurred. At that time, for a width of about five metres from shore there existed a mixture of grease and pancake ice and for the next twenty metres a mixture of frazil and grease ice. The spill occurred about 100 m offshore and was blown into the grease/pancake ice mixture by the wind and current of the river. At the time of observation no oil was visible within or above the grease ice and the only visible oil was that washed up on shore. The oil washed up on shore was grease ice that had been compressed and had the water forced from between the individual ice particles by the pressure of the ice against the shore. The result was a porous crystalline ice oil mixture that contained up to 50% oil. Figure 4.10 is a photograph of the ice-oil mixture which was observed at the shoreline. Samples of the oil were analyzed at the Environment Canada River Road Laboratory in Ottawa on a PARR densitometer. Table 4.7.1 provides a summary of the results. The specific gravity of the oil near freezing temperatures is quite close to that of the sea water at the spill site which was estimated to be 1.02. This raises the possibility that although there was no oil visible from above the grease and frazil ice there may have been large quantities of oil below or within the ice. There was also a high level of turbulence in the water during the period of the spill and hence it is possible that water/oil emulsions may have been formed.

Figure 4.10 Oil/Ice Mixture After Mantane Oil Spill

Table 4.7.1:

Temperature (°C)	DENSITY Sample 1	Sample 2
25	0.9996	1.0020
20	1.0033	1.0061
15	1.0073	1.0098
0	1.0178	1.0204

5. DISCUSSION

The experiments performed in this study have indicated that it is quite possible for significant quantities of oil to be entrained within a developing ice field. It also appears that there are many factors which contribute to determining the actual extent of oil entrainment.

The entire phenomenon of oil/ice interactions may be divided into two basic areas. First is an oil spill on open water and the subsequent development of ice beneath it. Second is spillage of a quantity of oil into an already formed or developing ice field. Experiments performed on the rate of ice formation beneath a static layer of oil in a related study (Cross et al. 1986) revealed that the oil insulates the water below from the cold environment and hence retards ice formation. It was observed that a layer of oil may act thermally as a layer of ice fifteen times its thickness. The nature of the structure of the ice remains unchanged. This effect applies for an oil layer beneath an already formed layer of ice as well as for a non-disturbed oil layer on the surface of the water. However, the likelihood of a static ocean environment seems remote. If the seas are turbulent, as would be expected, it appears that the waves will tend to break up the slick and negate its insulating effect. It has been suggested by some authors that the layer of oil would prove to act as a wave dampening force and hence promote ice formation. However experimental observations again tend to show that it would require a very thick or a very viscous layer of oil in order to accomplish this. It seems likely that even if this were to occur the ice

promoting effect would be negated by the thermally insulating effect of the intact oil layer.

The actual nature of the ice formed does not appear to change significantly in the presence of oil. Under static conditions normal columnar ice growth occurs beneath the oil. Under turbulent conditions the frazil to grease to pancake chain of ice growth occurs except that depending upon the nature of the oil and the level of turbulence, oil may become trapped between individual particles or as droplets in the pancake or columnar ice. Hence the resulting ice sheet as a whole is altered in that it then contains oil filled discontinuities.

The alternative to ice formation beneath a previously spilled oil layer is for an oil layer to be spilled or drift into an already developing ice field. The area of immediate concern is the introduction of oil to frazil, grease and pancake ice fields and not the natural progression which would be to investigate oil behaviour in leads or between large floes. The key question then, from a countermeasures or modelling point of view, is to determine how much oil will become entrained, and hence removed from sight, and under what circumstances will this occur. It is not surprising that the prime determinant of the extent of oil entrainment is the buoyancy of the oil. Because ice has a specific gravity of approximately 0.917 a frazil or grease ice and sea or fresh water mixture will have a net density signficantly less than that of sea water alone. Consequently, an oil will not have to be as dense to become submerged in a grease ice field as it would in water alone. The ice will float on the oil surface. Also, because of the interfacial

tension between oil and water particles as well as high oil viscosities an oil which is less dense than the net density of the grease/water mixture may still remain submerged within the grease ice layer. This was demonstrated by the results from the oil incorporation experiments where an oil of specific gravity 0.790 was incorporated below the surface to an extent as large as 50% oil entrainment.

Also of importance was the observation that ice particle size is a significant factor in determining the extent of oil incorporation. While the exact particle size could not be measured accurately it is reasonable to assume that there is a range of particle sizes about 2 to 5 mm in diameter or length where maximum oil incorporation occurs. It appears that there is a tradeoff between particle size and porosity of the ice field. Very large particles tend to have large spaces between them, and hence wide channels of water exist throughout the ice field through which a positively buoyant oil could easily surface. Conversely, very small particles may lead to lower porosity but it appears that individual oil drops experience strong enough buoyancy forces to push aside the tiny particles of ice and hence migrate back to the surface. There appears to be an optimum range where the spaces between ice particles are small enough to retard oil surfacing but the particles themselves are too large to be moved by individual oil drops and consequently large amounts of oil may be entrained. This is potentially of great importance because grease ice fields, while tending to achieve their own porosity and particle size are none-the-less susceptible to compaction by waves, ice floes, opening and closing of leads and land masses. Thus, at some point during the

compacting of grease ice the resulting coalescence of particles may pass through the stage of particle size and porosity conducive to high levels of oil entrainment. This implies that the dynamic action of a grease ice field may be instrumental in the incorporation of oil into ice.

Processes by which an oil could attain a sufficiently large density to allow submersion within an ice field were investigated. The oil incorporation experiments demonstrated that a density somewhat greater than that of ice itself is required for high extent of oil incorporation. The formation of oil emulsions are one method by which the net density of oil may be increased by its combination with denser sea water. Experiments showed that not only can this occur under subzero conditions but it may be accomplished in a reasonably short period of time. Furthermore, it may be possible for an oil/water/ice emulsion to be formed with a net density greater than that of ice.

Oil may also attain a higher density through weathering of the oil slick. In an ambient environment oils may significantly increase their density by evaporation of the light ends over a period of a few days. However, in very cold conditions the evaporation process becomes quite slow. There is some question as to whether an oil slick's life will be long enough to allow significant weathering for oil entrainment in ice. It is possible that an oil may be emulsified or incorporated in ice by other means long before weathering causes a noticeable change in the density of the oil. However, results from the actual spill observed in the Gulf of the St. Lawrence indicate appreciable density increases in

No. 6 fuel oil as a result of weathering over a period of only four days.

Turbulence is an important part of the mechanism by which oil may be entrained within a developing ice field. In the absence of ice it has been found, in earlier experiments by the author, that sufficient downward driving force may be created by breaking waves to balance the upwards buoyancy force acting on oil particles and hence entrain a portion of an oil slick beneath thesurface of the sea for indefinite periods of time. While a grease ice field would dampen waves experimental observations showed that sufficient agitation to force oil particles downward may easily be created. Once the oil particles have been forced downwards in the ice field they may remain there because of the same driving force or because of the natures of the ice field and oil. Observations of the spill of No. 6 fuel oil in the Gulf of the St. Lawrence reinforce this contention. In this case the grease ice field failed to prevent breaking of the waves and hence failed to prevent the resulting downward driving force of the waves. In light of the analysis of the oil from the spill and the revelation of its high density it seems likely that much of the spill was in fact incorporated amongst the grease ice field.

The experiments on the effect of solar radiation failed to quantify the effect of solar radiation on ice formation except to demonstrate that under static conditions a thin layer of oil may prevent ice from forming altogether as long as solar radiation is present and temperatures are only a few degrees below the freezing mark. However, it

seems likely that under turbulent conditions an oil slick would be sufficiently broken up to negate the effect of solar radiation on any subsequent ice formation. Solar radiation is more likely to play a role where there is a layer of oil on top of a solid ice layer. In such a case it could be expected that solar radiation would hasten the thawing process.

If it is established that oil may be entrained, under a given set of cirucmstances, within a grease ice layer and subsequently completely frozen into floes of pancake ice then the topic of rates of thaw and the effect of the oil upon the thaw process takes on a new importance. The experiments performedshowed that denser oils would take longer to be released from thawing ice than less dense oils because of their deeper entrainment within the ice and their tendency to have a neutral or smaller positive buoyancy than the lighter oils. As the oil is released and forms pools on the surface of the ice it is expected that the surface layer will begin to affect the thawing process as well, especially in the presence of solar radiation.

Thus, this study has demonstrated that large quantities of oil may be entrained within a developing ice field. The main factors influencing the entrainment are oil density and the level of turbulence within the ice field. It appears that given a sufficient data base on oil incorporation in ice and a thorough theoretical approach to the topic based on oil buoyancy, turbulent forces and oil/water/ice interfacial tensions a model may be developed which is capable of predicting the extent of oil entrainment expected in a developing ice field. Such a

model would require the input of all the relevant physical data on the oil spilled as well as sea and ice conditions. Having established the extent of oil incorporation such a model would then be able to predict the thaw behaviour of the oil and ice mixture.

6. CONCLUSIONS

A series of experiments have been performed which investigate the phenomenon of oil entrainment within a developing ice field. The observations recorded from the laboratory experiments have been complemented by observations from an actual oil spill during freezing conditions.

It is concluded that significant quantities of oil may be entrained within a developing ice field under freezing conditions. The extent of incorporation is enhanced by:

i) a high oil density occurring naturally or induced by weathering.

ii) the presence of sufficient energy to disperse the surface oil at an appreciable rate and induce mixing within the ice field.

iii) a high oil viscosity occurring naturally or induced by weathering.

iv) the formation of emulsions of sea water and/or ice in oil.

v) the formation of smaller oil droplets.

vi) the formation or coalescence of ice particles to a size of approximately 5mm in diameter.

It is concluded that under non-turbulent water conditions an oil layer will behave as an insulating layer and retard ice development beneath it. Under turbulent water conditions it is likely that the presence of oil will have a negligible effect on the development of ice except for its possible incorporation within the developing ice.

Furthermore it appears that solar radiation has little effect on the development of an ice field in the presence of oil unless environmental conditions are non-turbulent. In such a case solar radiation may significantly retard the ice formation process.

The least buoyant oils (of highest density) will require the greatest amount of time to be released from a frozen ice pancake during the thawing process. Once the oil begins to collect on the surface of the ice, solar radiation will tend to hasten the thawing process.

Finally, it has been suggested that an empirical and theoretical approach be taken to model the process of oil incorporation within a developing ice field in order to predict the extent of oil entrainment under given circumstances.

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